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(54) Silver halide photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material is disclosed. The light-sensitive material comprisescomprises
a support,
a hydrophilic colloid layer and a silver halide emulsion layer provided on a side of said support and
a hydrophilic colloid layer provided on the back side of said support opposite to the surface the emulsion layer provided thereon,
wherein the layer arranged at the outermost portion of the emulsion provided side of the support contains
a kind of irregular-shaped matting agent having a particle size of less than 4 μm in an amount of from 4 mg/m^2 to 80 mg/m^2, and
a kind of regular-shaped or iregular-shaped matting agent having a size of not less than 4 μm in an amount of from 4 mg/m^2 to 80 mg/m^2, and
the outer surface of said layer arranged at the outermost portion of the emulsion provided side of the support has a surface smoothness degree of not less than 25 mmHg.

The light-sensitive material is suitable for graphic arts use and has a highly matted surface for improving the ability of contact in a vacuum printing apparatus and top/back surface differentiation.

SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material for graphic art use, more specifically to a silver halide photographic light-sensitive material for graphic art exposed while being kept in contact with a plate-shapped member, or a sheet such as a photographic film or paper.

BACKGROUND OF THE INVENTION

In the film working in a photomechanical process, a vacuuming time of 15 to 30 seconds in each exposure is usually required to bring a film into vacuum contact with a printer or camera, which accounts for a considerable ratio of the exposure procedure. Thus, vacuuming time should be shortened to improve working efficiency.

Traditionally, vacuum contact ability of a photographic material has been improved by increasing the matting degree of surface using a matting agent of large particle size, since any matting agent of small particle size has no satisfactory effect. However, this conventional method has shortcomings of pinhole formation, reduction of image density in practice and other problems due to sinking of matting agent in the coated layer. Also, a procedure has been followed to clearly differentiate the top and back of the processed film in which an irregular-shaped matting agent is used in the emulsion layer side of the support and a regular-shaped matting agent is used on the backing layer side to make the top and back surfaces different from each other with respect to glossiness. However, there has been a limitation on the amount of addition of an irregular-shaped matting agent, since transparency loss increases as the amount of its use increases.

There is another drawback that static charge of film leads to adhesion of dust, and easily causes unsharpness of printed images.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a silver halide photographic light-sensitive material which has an increased degree of matting without transparency loss and image density reduction, minimized pinhole formation, and high top-back differentiation ability after processing. It is another object of the present invention to provide a silver halide photographic light-sensitive material prevented from static charge.

The objects of the present invention described above are accomplished by a silver halide photographic light-sensitive material comprising a support, a hydrophilic colloid layer and a silver halide emulsion layer provided on a surface of the support and a hydrophilic colloid layer provided on the back surface of the support opposite to the emulsion provided surface, wherein the layer arranged at the outermost portion of the emulsion provided side of the support contains a first kind of irregular-shaped matting agent having a particle size of less than 4 μm in an amount of from 4 mg/m^2 to 80 mg/m^2, and a second kind of regular-shaped or iregular-shaped matting agent having a size of not less than 4 μm in an amount of from 4 mg/m^2 to 80 mg/m^2, and the outer surface of the layer arranged at the outermost portion of the emulsion provided side of the support has a surface smoothness degree of not less than 25 mmHg.

The surafce smoothness degree is a value measured by the method defined in "JAPAN TAPPI Test Method for Paper and Pulp No. 5-74" using an air-micrometer type testing apparatus.

It is preferable that the outermost hydrophilic colloidal layer on the back side contains a regular-shaped matting agent and 0 to 15 mg/m^2 of an irregular-shaped matting agent and has a surface smoothness value of not more than 200 mmHg.

It is also preferable that the surface resistivity on the back side is not more than 1.0 x 10^{12} Ωcm^{-2}

Also, for obtaining a high contrast for a graphic art photographic material, it is preferable that the light-sensitive material of the present invention contains a tetrazolium compound and/or a hydrazine compound, and it is also preferable that the hydrophilic colloid contained in the outermost layer on the silver halide emulsion layer side is gelatin and is dried under such conditions that average surface temperature is not more than 20°C when the weight ratio of water and gelatin in the entire coating solution on the surface becomes 400% during coating and drying.

DETAILED DESCRIPTION OF THE INVENTION

Any known matting agent can be used for the present invention. Examples of usable matting agents include inorganic substance particles such as the silica described in Swiss Patent No. 330,158, the glass powder described in French Patent No. 1,296,995, and the carbonates of alkaline earth metals, cadmium, zinc, described in British Patent No. 1,173,181; and organic substance particles such as the starch described in US Patent No. 2,322,037, the starch derivatives described in Belgian Patent No. 625,451 or British Patent No. 981,198, the polyvinyl alcohol described in Japanese Patent Examined Publication No. 3643/1969, the polystyrene or polymethyl methacrylate described in Swiss Patent No. 330,158, the polyacrylonitrile described in US Patent No. 3,079,257 and the polycarbonate described in US Patent No. 3,022,169.

In the present invention, these matting agents may be used singly or in combination. Although the regular-shaped matting agent used for the present invention is preferably in a spherical form, any other form such as a tabular form or a cubic form is acceptable, as long as the matting agent comprises particles being uniform. On the other hand, irregular-shaped matting agents include not only those comprising a single form but also those comprising a number of different forms and those whose shape itself is irregular. In the present invention, the grain size of a matting agent is expressed as the diameter of a sphere converted from the volume of the matting agent.

In the present invention, the outermost layer on the emulsion layer side contains a first kind of irregular-shaped matting agent of less than 4 μm in particle size and a second kind of regular-shaped and/or irregular-shaped matting agent of not less than 4 μm in grain size in a ratio of 4 to 80 mg/m^2 preferably 4 to 30 mg/m^2.

The size of the first kind of the matting agent is preferably within the range of from 1.0 μm to less than 4 μm, and that of the second kind of matting agent is preferably within the range of from 4 μm to 17 μm. The surface smoothness degree of this layer is not less than 25 mmHg and preferably within the range of 25 to 200 mmHg.

It is preferable that the outermost layer on the side containing no emulsion layer contains a kind of regular-shaped matting agent in an amount of 4 to 80 mg/m^2 and an irregular-shaped matting agent in an amount of 0 to 15 mg/m^2, and has a surface smoothness degree of not more than 200 mmHg, preferably 25 to 200 mmHg.

To ensure the basic function of the matting agent, it is desirable that part of the matting agent is exposed to open air. The exposed portion of the matting agent may part or all of the matting agent added. The matting agent may be added by the method in which the matting agent is coated after being dispersed in a coating solution or by the method in which the matting agent is sprayed on the coated surface of the coating solution before completion of drying it. These two methods may be used in combination, when a number of different matting agents are added.

The surface smoothness degree used in the present invention are measured according to the fore-mentioned JAPAN TAPPI Test Method No. 5-74 using SMOOSTAR SM-6B, produced by Toei Denshi Kogyo KK.

In coating, drying is achieved normally by dry air blowing, but the other means such as far infrared rays, microwaves, may be used for drying. When the outermost layer on the silver halide emulsion layer side is coated, it is particularly preferable that the average surface temperature is not more than 20°C when the ratio by weight of water and gelatin becomes 400% with respect to the entire coating solution for a single or number of layers coated.

It is preferable that the surface resistivity of the side having no silver halide emulsion layer of the light-sensitive material (hereinafter referred to as backing layer) is not more than 1.0 x 10^{12} Ωcm^{-2}, more preferably not more than 8 x 10^{11} Ωcm^{-2}. Having such a surface resistivity on the backing side prevents dust adhesion and thus improves vacuum contact.

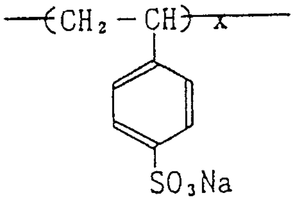
For this reason, it is preferable to form an antistatic layer, which comprises a reaction product of 1) a water-soluble electroconductive polymer, 2) hydrophobic polymer particles and 3) a hardener, on the surface on the side containing no light-sensitive silver halide emulsion layer of the support. It is also preferable that the hydrophobic polymer particles added to the antistatic layer are dispersed and stabilized with a nonionic surfactant having three or more alkylene oxide groups.

The above water-soluble electroconductive polymer is capable of forming a transparent layer even when it is used alone, but it causes layer cracking due to drying condition fluctuation. In the above configuration, hydrophobic polymer grains are contained to prevent this cracking phenomenon, and their effect is significant.

Examples of the water-soluble electroconductive polymer preferably used in the light-sensitive material of the present invention include polymers having a electroconductive group such as a sulfonic acid group, a sulfate group, a quaternary ammonium salt, a tertiary ammonium salt and a polyethylene oxide group. Among these groups, a sulfonic acid group, a sulfate group and a quaternary ammonium salt are particularly preferable. The electroconductive group is preferably required in a ratio of not less than 5% by weight per polymer molecule. The polymer has a molecular weight of 3000 to 100000, preferable 3500 to 50000.

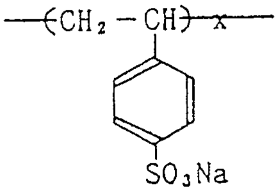
Examples of water-soluble electroconductive polymer compounds usable in the present invention are given below, but these are not to be construed as limitative.

A - 1 Homopolymer



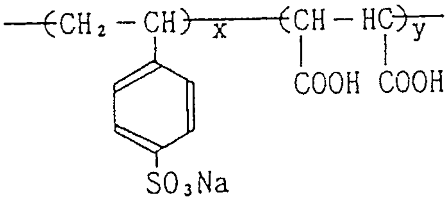
$\bar{M} \fallingdotseq 60000$

A - 2 Homopolymer



$\bar{M} \fallingdotseq 70000$

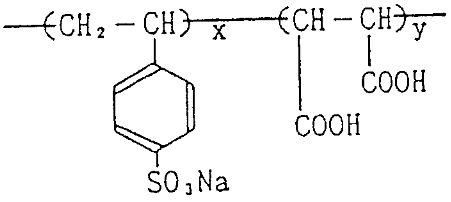
A - 3



$X:Y = 67:34$

$\bar{M} \fallingdotseq 5000$

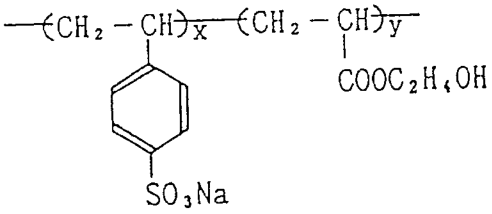
A - 4



$X:Y = 50:50$

$\bar{M} \fallingdotseq 12000$

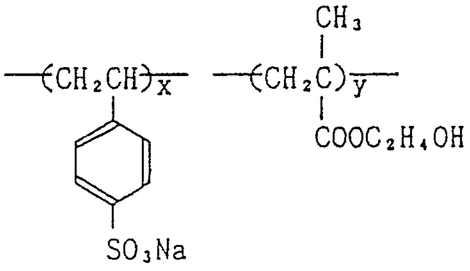
A - 5



$x:y = 70:30$

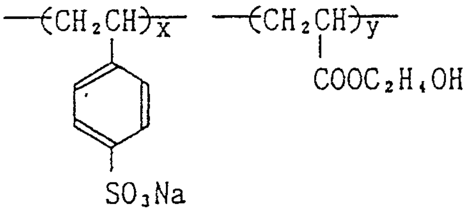
$\bar{M} \fallingdotseq 5000$

A - 6



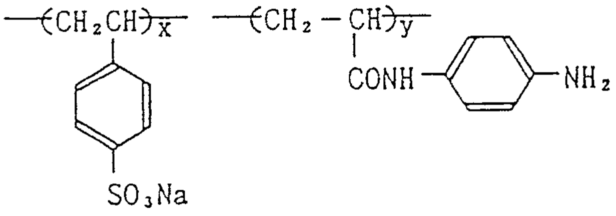
x : y = 90 : 10
Mn = 10000

A - 7



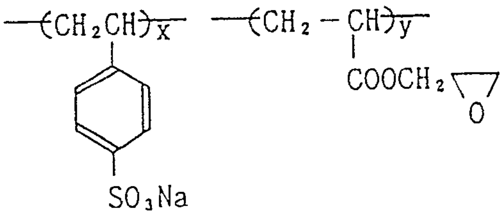
x : y = 60 : 40
Mn = 7000

A - 8



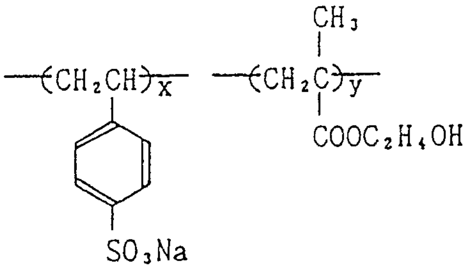
x : y = 90 : 10
Mn = 15000

A - 9



x : y = 60 : 40
Mn = 5000

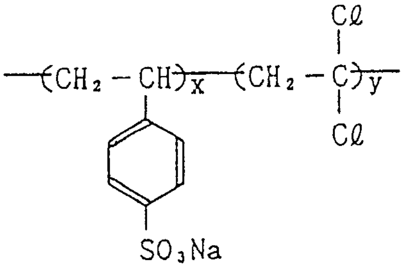
A − 10



$x:y = 90:10$

$Mn = 20000$

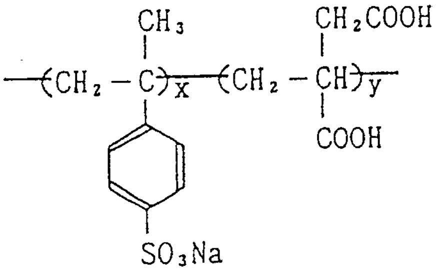
A − 11



$x:y = 97:3$

$\overline{M} \fallingdotseq 30000$

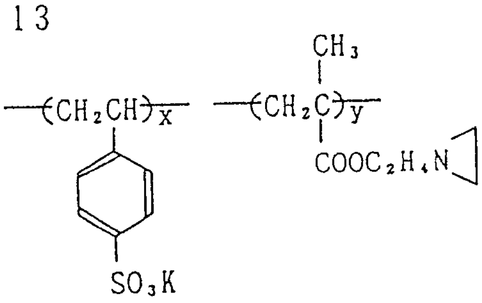
A − 12



$x:y = 98:2$

$\overline{M} \fallingdotseq 5000$

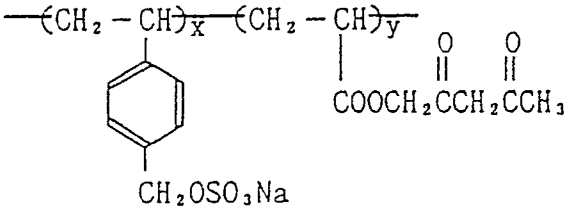
A − 13



$x:y = 60:40$

$Mn = 8000$

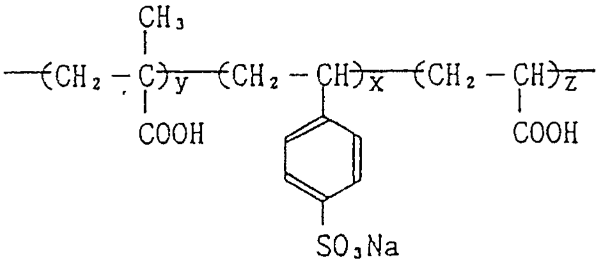
A − 14



$x:y = 95:5$

$\overline{M} \fallingdotseq 25000$

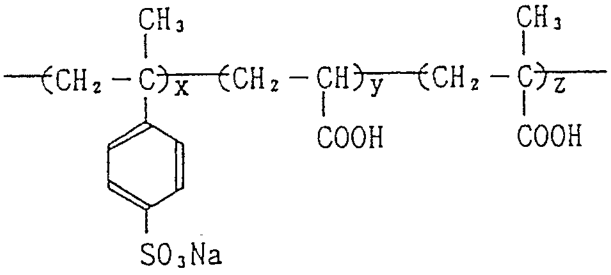
A − 15



$x:y:z = 80:19:1$

$\overline{M} \fallingdotseq 5000$

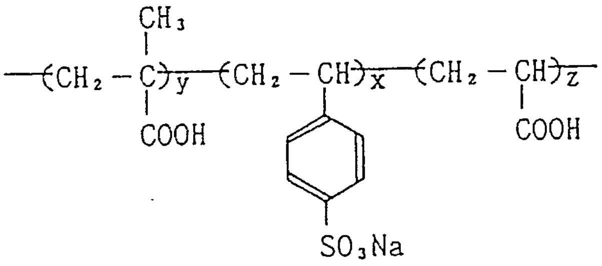
A − 16



$x:y:z = 70:28:2$

$\overline{M} \fallingdotseq 6000$

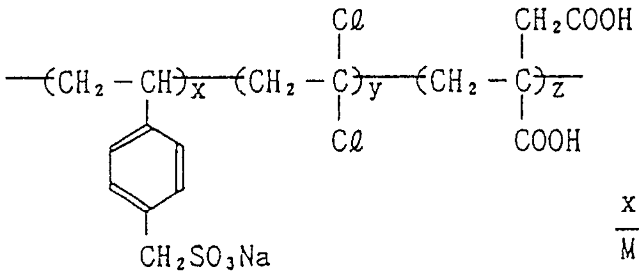
A − 17



$x:y:z = 85:13:2$

$\overline{M} \fallingdotseq 8000$

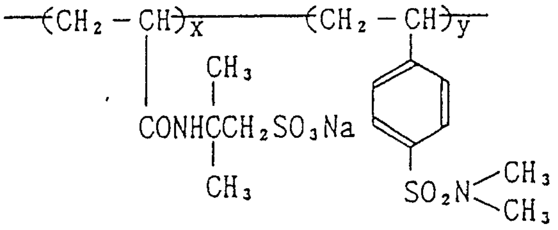
A - 18



$x:y:z = 80:16:4$

$\overline{M} \fallingdotseq 10000$

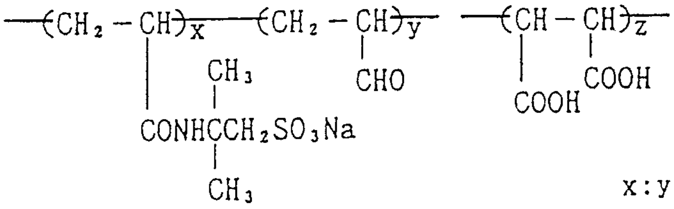
A - 19



$x:y = 90:10$

$\overline{M} \fallingdotseq 30000$

A - 20

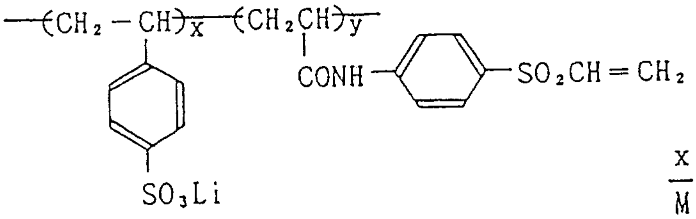


$$-(CH_2-\underset{CONH\underset{CH_3}{\overset{CH_3}{C}}CH_2SO_3Na}{CH})_x-(CH_2-\underset{CHO}{CH})_y-(\underset{COOH}{CH}-\underset{COOH}{CH})_z-$$

$x:y:z = 85:10:5$

$\overline{M} \fallingdotseq 10000$

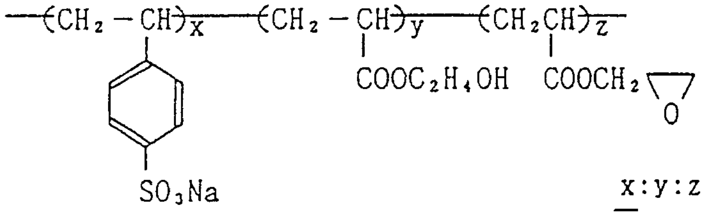
A - 21



$x:y = 90:10$

$\overline{M} \fallingdotseq 6000$

A − 22



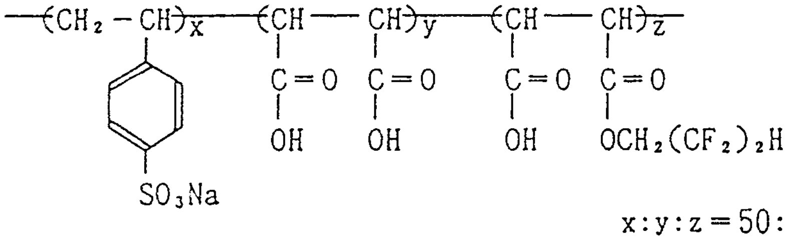
$x:y:z = 80:10:10$

$\overline{M} \fallingdotseq 15000$

A − 23 Dextran sulfate

Degree of substitution

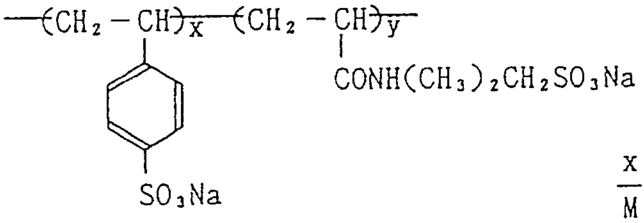
A − 24



$x:y:z = 50:40:10$

$\overline{M} \fallingdotseq 100000$

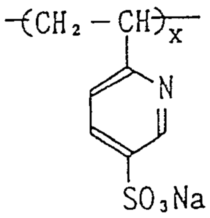
A − 25



$x:y = 80:20$

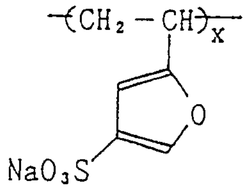
$\overline{M} \fallingdotseq 50000$

A − 26



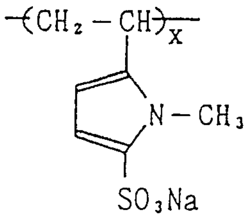
$\overline{M} \fallingdotseq 100000$

A - 27



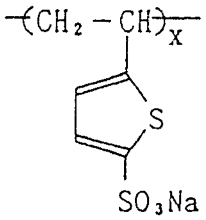
$\bar{M} \fallingdotseq 20000$

A - 28



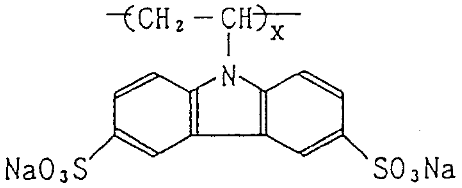
$\bar{M} \fallingdotseq 20000$

A - 29



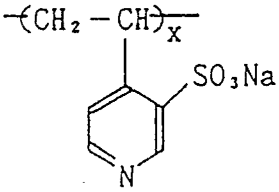
$\bar{M} \fallingdotseq 150000$

A - 30



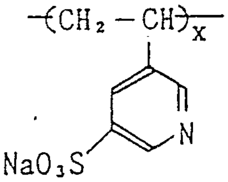
$\bar{M} \fallingdotseq 300000$

A － 31



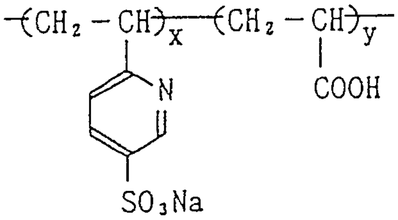
$\bar{M} \fallingdotseq 280000$

A － 32



$\bar{M} \fallingdotseq 50000$

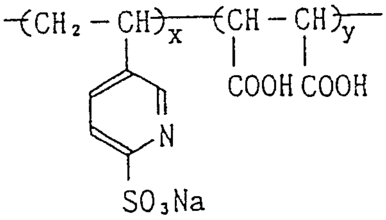
A － 33



x ： y＝60 ： 40

$\bar{M} \fallingdotseq 80000$

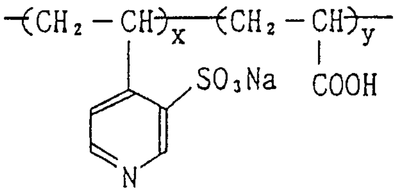
A － 34



x ： y＝70 ： 30

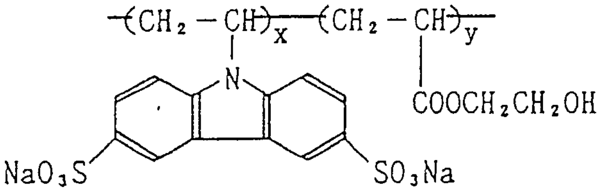
$\bar{M} \fallingdotseq 5000$

A − 35



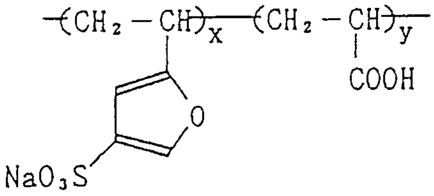
$x : y = 80 : 20$
$\bar{M} \fallingdotseq 50000$

A − 36



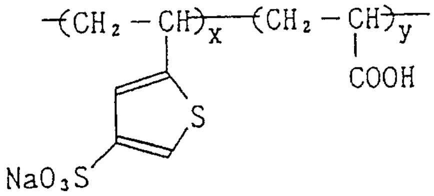
$x : y = 75 : 25$
$\bar{M} \fallingdotseq 40000$

A − 37



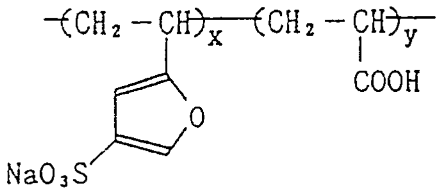
$x : y = 80 : 20$
$\bar{M} = 60000$

A − 38



$x : y = 90 : 10$
$\bar{M} \fallingdotseq 40000$

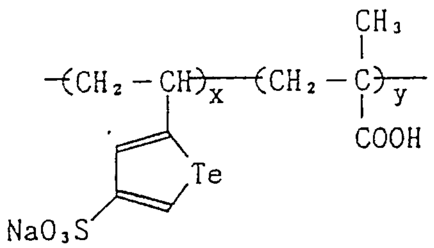
A − 39



$x : y = 55 : 45$

$\bar{M} \fallingdotseq 20000$

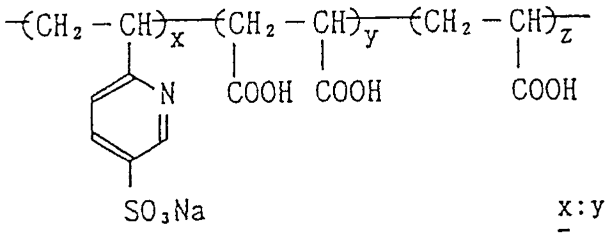
A − 40



$x : y = 90 : 10$

$\bar{M} = 60000$

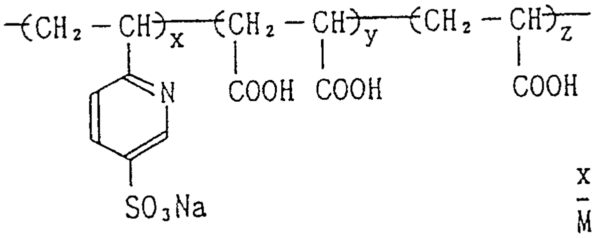
A − 41



$x : y : z = 80 : 10 : 10$

$\bar{M} \fallingdotseq 10000$

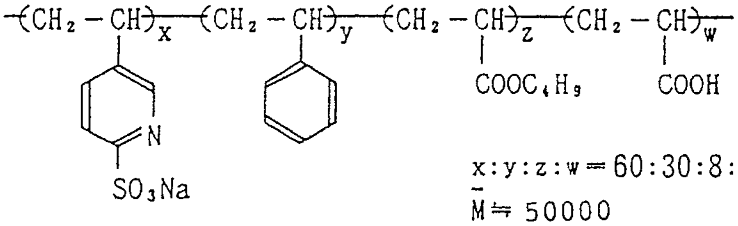
A − 42



$x : y : z = 70 : 25 : 5$

$\bar{M} \fallingdotseq 30000$

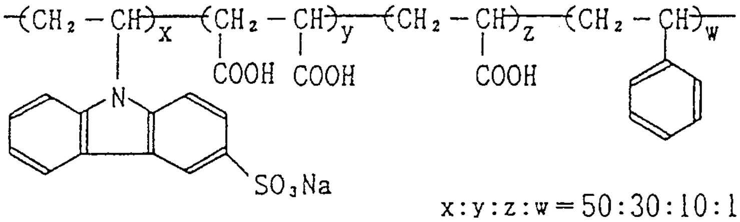
A − 43



$x:y:z:w = 60:30:8:2$

$\bar{M} \fallingdotseq 50000$

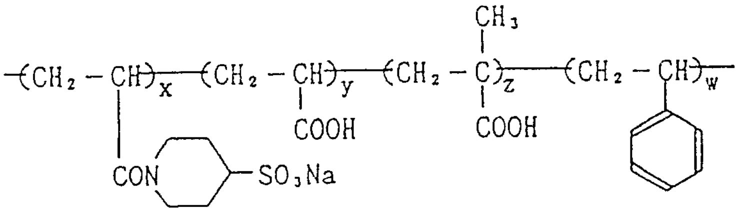
A − 44



$x:y:z:w = 50:30:10:10$

$\bar{M} \fallingdotseq 60000$

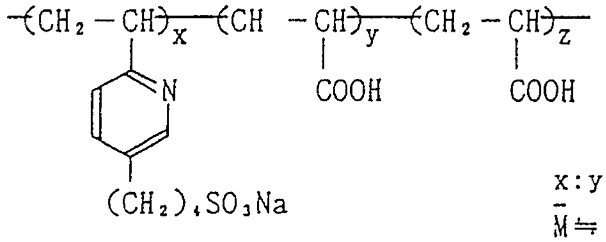
A − 45



$x:y:z:w = 40:30:20:10$

$\bar{M} \fallingdotseq 50000$

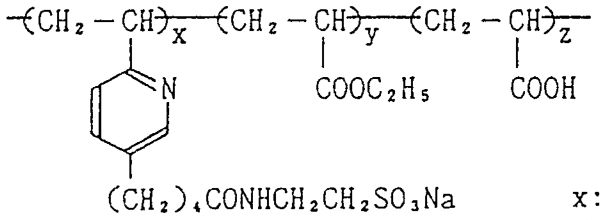
A − 46



x:y:z = 60:30:10

$\bar{M}$ ≒ 30000

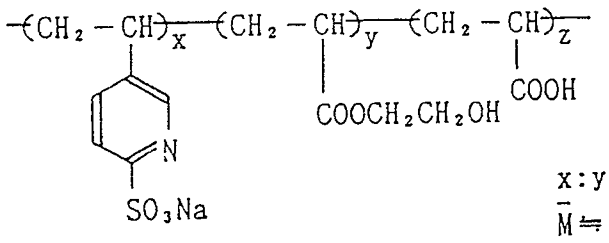
A − 47



x:y:z = 80:5:15

$\bar{M}$ ≒ 50000

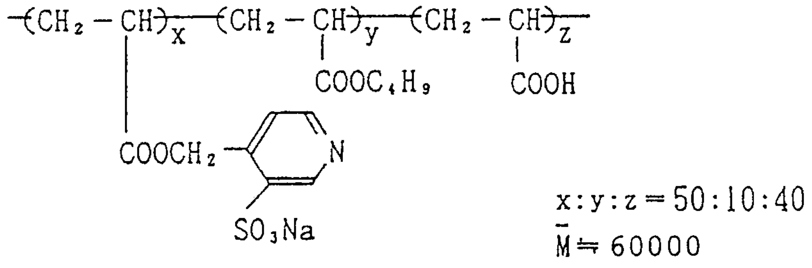
A − 48



x:y:z = 55:35:10

$\bar{M}$ ≒ 30000

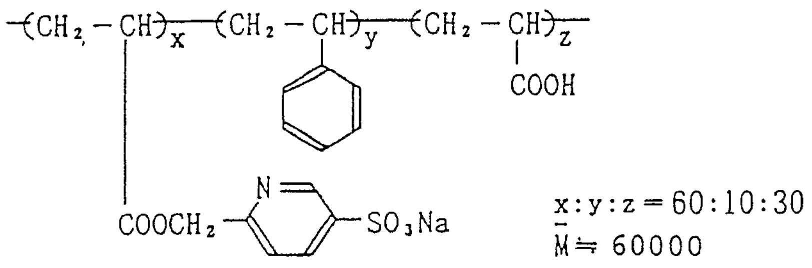
A - 49



x:y:z=50:10:40

$\bar{M} \fallingdotseq 60000$

A - 50



x:y:z=60:10:30

$\bar{M} \fallingdotseq 60000$

In (A-1) through (A-50) shown above, x, y and z represent the mol% ratios of respective monomer components and $\overline{M}$ represents the average molecular weight (in the present specification, average molecular weight means number-average molecular weight).

These polymers can be synthesized by polymerizing a commercially available monomer or a monomer obtained by an ordinary method. The amount of addition of these compounds is preferably 0.01 to 10 g/m^2, more preferable 0.1 to 5 g/m^2.

The hydrophobic polymer particles added to the water-soluble electroconductive polymer layer are in the form of a latex which are substantially insoluble in water. This hydrophobic polymer is obtained by polymerizing any combination of monomers selected from acrylamide derivatives and methacrylamide derivatives. It is preferable that an acrylamide derivative or a methacrylamide derivative is contained in a ratio of at least 0.1 mol%, with further preference given to a concentration of not less than 1 mol%.

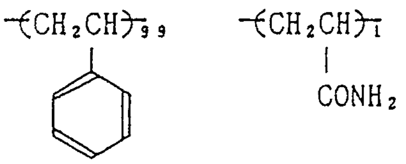
There are two methods of preparing a hydrophobic polymer as a latex. One is emulsion polymerization and the other is dissolution and microdispersion of the solid polymer in a low boiling solvent, followed by solvent distillation. Emulsion polymerization is preferred, since finer and uniform grain size is obtained.

An nonionic surfactant having 3 or more alkylene oxide groups is preferably used for emulsion polymerization. The preferable ratio of the surfactant is not more than 10% by weight to the monomer. Excessive us of the surfactant may cause clouding in the electroconductive layer.

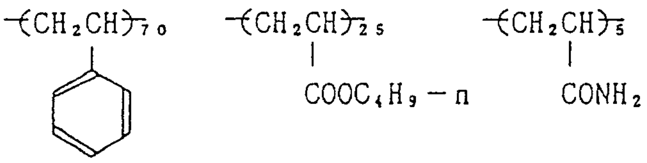
The molecular weight of the hydrophobic polymer should exceed 3000, and there is almost no difference in transparency among molecular weights.

Examples of the hydrophobic polymer of the present invention are given below.

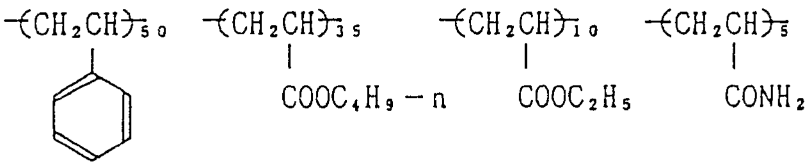
B − 1



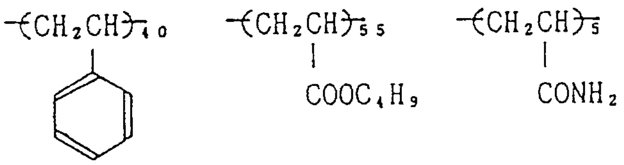
B − 2



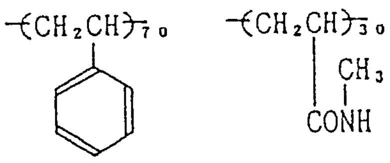
B − 3



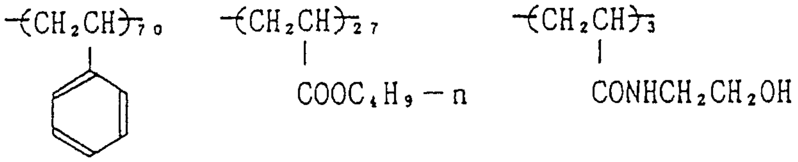
B − 4



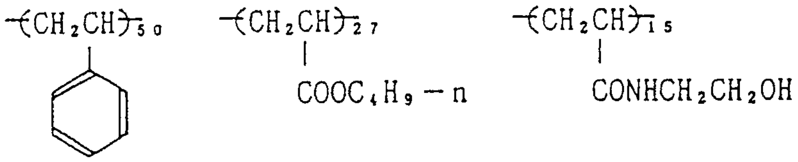
B − 5



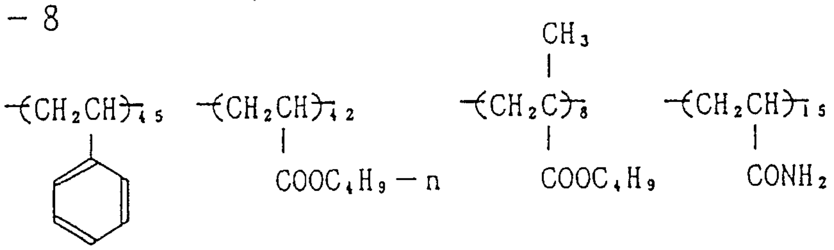
B－6



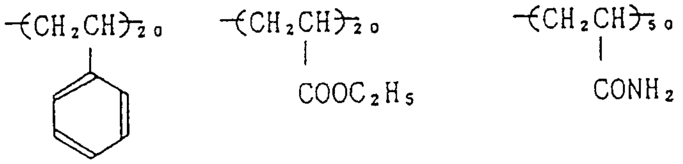
B－7



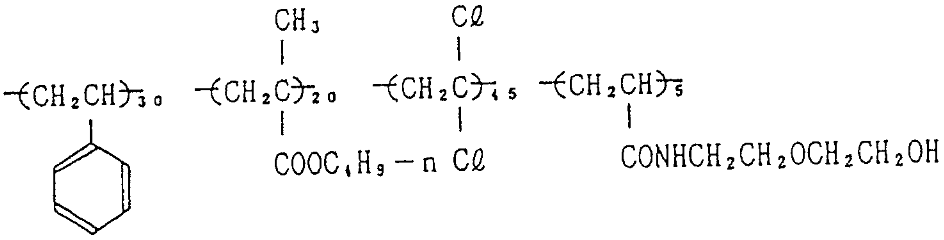
B－8



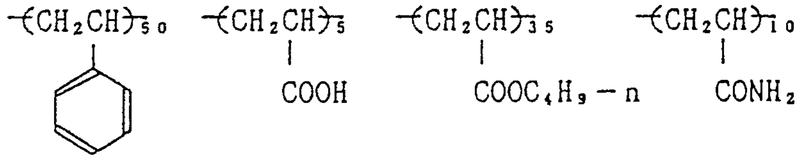
B－9



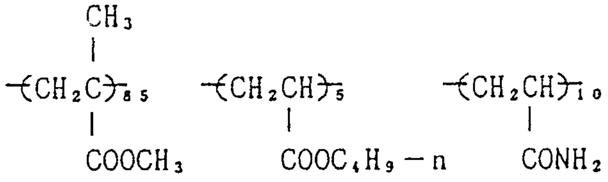
B－10



B－11

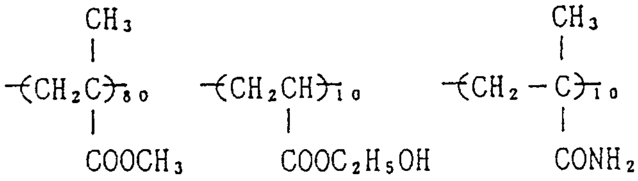


B－12



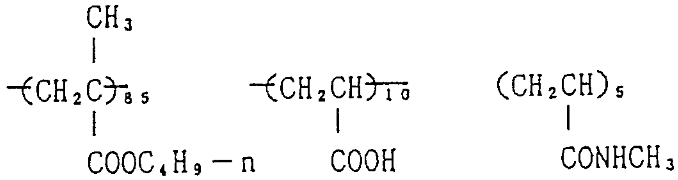
$$\underset{COOCH_3}{\overset{CH_3}{-(CH_2C)_{85}}}\quad \underset{COOC_4H_9-n}{-(CH_2CH)_5}\quad \underset{CONH_2}{-(CH_2CH)_{10}}$$

B－13



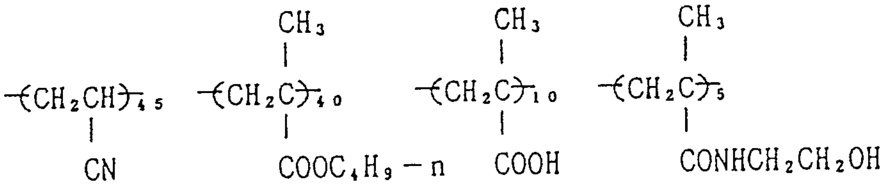
$$\underset{COOCH_3}{\overset{CH_3}{-(CH_2C)_{80}}}\quad \underset{COOC_2H_5OH}{-(CH_2CH)_{10}}\quad \underset{CONH_2}{\overset{CH_3}{-(CH_2-C)_{10}}}$$

B－14



$$\underset{COOC_4H_9-n}{\overset{CH_3}{-(CH_2C)_{85}}}\quad \underset{COOH}{-(CH_2CH)_{10}}\quad \underset{CONHCH_3}{(CH_2CH)_5}$$

B－15



$$\underset{CN}{-(CH_2CH)_{45}}\quad \underset{COOC_4H_9-n}{\overset{CH_3}{-(CH_2C)_{40}}}\quad \underset{COOH}{\overset{CH_3}{-(CH_2C)_{10}}}\quad \underset{CONHCH_2CH_2OH}{\overset{CH_3}{-(CH_2C)_5}}$$

The electroconductive layer is coated on a transparent support. Any transparent photographic support can be used, but it is preferable to use a polyethylene terephthalate or cellulose triacetate support prepared to have a visible light transmittance of not less than 90%.

These transparent supports are prepared by a method obvious to those skilled in the art, but as the case may be, they may be colored blue by the addition of a small amount of a dye without substantial inhibition of light transmission.

The support of the present invention may be coated with a subbing layer containing a latex polymer after corona discharge treatment. It is preferable that corona discharge treatment be carried out at an energy level of 1 mW to 1 kW/m^2 min. It is particularly preferable to carry out corona discharge treatment again before the electroconductive layer is coated after the latex subbing layer is coated.

The compound for hardening the electroconductive layer of the present invention is preferably a polyfunctional aziridine, with particular preference given to a bifunctional or trifunctional aziridine having a molecular weight of not more than 600.

The electroconductive layer of the present invention may be located on the support side from the light-sensitive layer or on the side opposite to the light-sensitive layer, i.e., the back of the support.

A nonionic surfactant is used as a dispersant in the electric conductive layer, with preference given to a polyalkylene oxide compound.

As the above polyalkylene oxide compound, a compound having at least 3 and at most 500 polyalkylene oxide groups in its molecular structure, and it can be synthesized by condensation of polyalkylene oxide with a compound having an active hydrogen atom such as an aliphatic alcohol, a phenol, a fatty acid, an aliphatic mercaptan or an organic amine, or by condensation of a polyol such as polypropylene glycol or a polyoxytetramethylene polymer with, for example, an aliphatic mercaptan, an organic amine, ethylene oxide or propylene oxide.

The polyalkylene oxide compound described above may be a block copolymer wherein the polyalkylene oxide chain in its molecular structure has been divided into two or more portions.

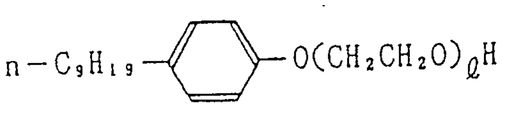
In this case, it is preferable that the overall degree of polymerization of the polyalkylene oxide is not less than 3 and not more than 100.

Examples of the polyalkylene oxide compound described above for arbitrary use for the present invention are given below.

[Example compounds]

[Ao - 1] $HO(CH_2CH_2O)nH$ [n = 4]
[Ao - 2] $HO(CH_2CH_2O)nH$ [n = 35]
[Ao - 3] $HO(CH_2CH_2O)nH$ [n = 135]
[Ao - 4] $HO(CH_2CH_2O)nH$ [n = 225]
[Ao - 5] $HO(CH_2CH_2O)nH$ [n = 450]
[Ao - 6] $n\text{-}C_4H_9O(CH_2CH_2O)_\ell H$ [ℓ = 20]
[Ao - 7] $n\text{-}C_8H_{17}O(CH_2CH_2O)_\ell H$ [ℓ = 30]
[Ao - 8] $n\text{-}C_{12}H_{25}O(CH_2CH_2O)_\ell H$ [ℓ = 30]

〔Ao - 9〕



〔ℓ = 30〕

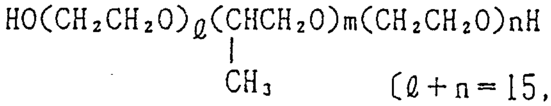
〔Ao - 10〕 $n-C_{12}H_{25}S(CH_2CH_2O)\ H$ 〔ℓ = 30〕

〔Ao - 11〕 $C_4H_9S(CH_2CH_2O)nCOCH_2CH_2COOH$ 〔n = 50〕

〔Ao－12〕 $HO(CH_2CH_2O)_{\ell}(CH_2)m(CH_2CH_2O)nCOCH_2CH_2COOH$

〔$\ell+n=70$, $m=5$〕

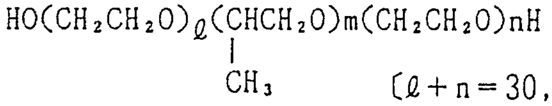
〔Ao－13〕



$HO(CH_2CH_2O)_{\ell}(\underset{\underset{CH_3}{|}}{C}HCH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=15$, $m=17$〕

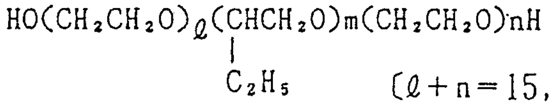
〔Ao－14〕



$HO(CH_2CH_2O)_{\ell}(\underset{\underset{CH_3}{|}}{C}HCH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=30$, $m=35$〕

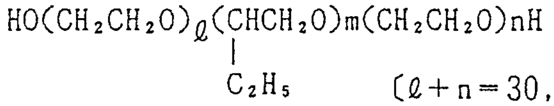
〔Ao－15〕



$HO(CH_2CH_2O)_{\ell}(\underset{\underset{C_2H_5}{|}}{C}HCH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=15$, $m=15$〕

〔Ao－16〕



$HO(CH_2CH_2O)_{\ell}(\underset{\underset{C_2H_5}{|}}{C}HCH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=30$, $m=15$〕

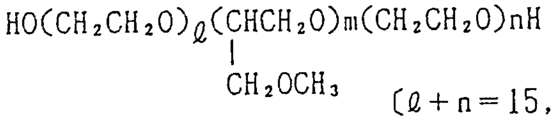
〔Ao－17〕 $HO(CH_2CH_2O)_{\ell}(CH_2CH_2CH_2CH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=23$, $m=21$〕

〔Ao－18〕 $HO(CH_2CH_2O)_{\ell}(CH_2CH_2CH_2CH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=38$, $m=15$〕

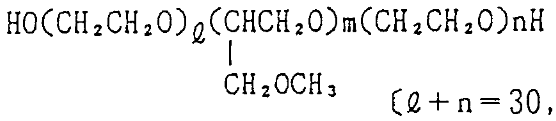
〔Ao－19〕



$HO(CH_2CH_2O)_{\ell}(\underset{\underset{CH_2OCH_3}{|}}{C}HCH_2O)m(CH_2CH_2O)nH$

〔$\ell+n=15$, $m=15$〕

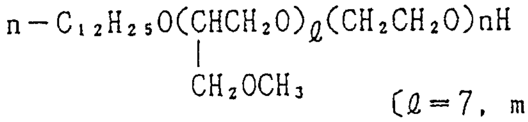
〔Ao－20〕



$$HO(CH_2CH_2O)_{\ell}(\underset{CH_2OCH_3}{\underset{|}{C}}HCH_2O)m(CH_2CH_2O)nH$$

〔$\ell+n=30$, $m=15$〕

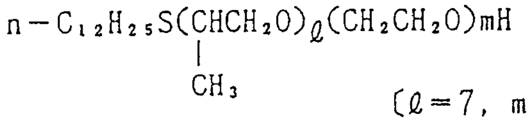
〔Ao－21〕



$$n-C_{12}H_{25}O(\underset{CH_2OCH_3}{\underset{|}{C}}HCH_2O)_{\ell}(CH_2CH_2O)nH$$

〔$\ell=7$, $m=30$〕

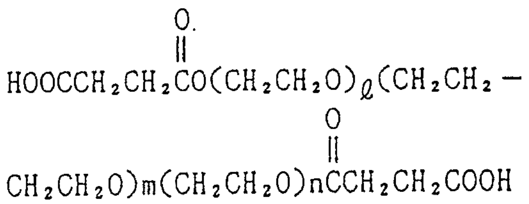
〔Ao－22〕



$$n-C_{12}H_{25}S(\underset{CH_3}{\underset{|}{C}}HCH_2O)_{\ell}(CH_2CH_2O)mH$$

〔$\ell=7$, $m=30$〕

〔Ao－23〕

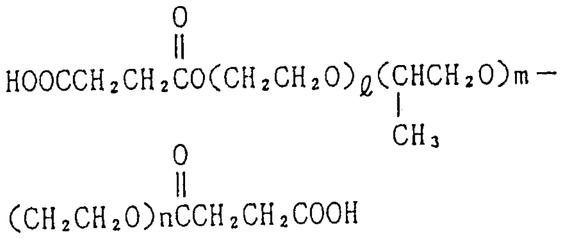


$$HOOCCH_2CH_2\overset{\overset{O}{\|}}{C}O(CH_2CH_2O)_{\ell}(CH_2CH_2-$$

$$CH_2CH_2O)m(CH_2CH_2O)n\overset{\overset{O}{\|}}{C}CH_2CH_2COOH$$

〔$\ell+n=15$, $m=15$〕

〔Ao－24〕

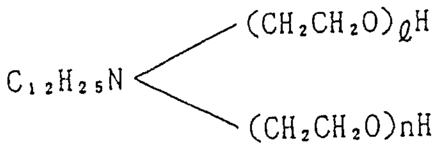


$$HOOCCH_2CH_2\overset{\overset{O}{\|}}{C}O(CH_2CH_2O)_{\ell}(\underset{CH_3}{\underset{|}{C}}HCH_2O)m-$$

$$(CH_2CH_2O)n\overset{\overset{O}{\|}}{C}CH_2CH_2COOH$$

〔$\ell+n=15$, $m=20$〕

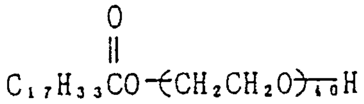
〔Ao－25〕



$$C_{12}H_{25}N\begin{cases}(CH_2CH_2O)_{\ell}H\\(CH_2CH_2O)nH\end{cases}$$

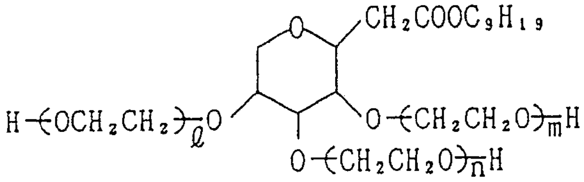
〔$\ell+n=30$〕

[Ao-26]



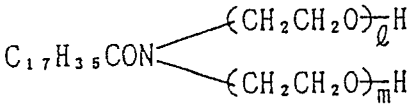
$$C_{17}H_{33}\overset{\overset{O}{\|}}{C}O\text{-}(CH_2CH_2O)_{10}H$$

[Ao-27]



$\ell+m+n=20$

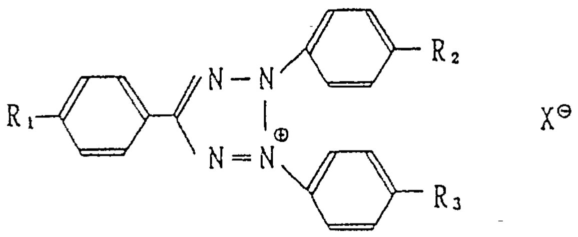
[Ao-28]



$\ell+m=12$

A tetrazolium compound represented by the following Formula I can be used in the light-sensitive material of the present invention.

Formula I

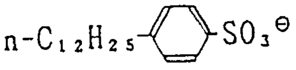


With respect to the Formula I shown above, examples of preferable substituents represented by R_1 through R_3 include an alkyl group such as methyl, ethyl, cyclopropyl, propyl, isopropyl, cyclobutyl, butyl, isobutyl, pentyl and cyclohexyl group, an amino group, an acylamino group such as acetylamino group, a hydroxyl group, an alkoxy group such as methoxy, ethoxy, propoxy, butoxy and pentoxy group, an acyloxy groups such as acetyloxy group, a halogen atoms such as fluorine, chlorine and bromine atom, a carbamoyl group, an acylthio group such as acetylthio group, an alkoxycarbonyl group such as ethoxycarbonyl group, a carboxyl group, acyl group such as acetyl group, a cyano group, a nitro group, a mercapto group, a sulfoxy group and an aminosulfoxy group.

Examples of the anion represented by $X^{\ominus}$ include halogen ions such as chlorine ion, bromine ion and iodine ion; acid radicals of inorganic acids such as nitric acid, sulfuric acid and perchloric acid; acid radicals of organic acids such as sulfonic acid and carboxylic acid; and anionic surfactants, specifically lower alkylbenzenesulfonic acid anions such as p-toluenesulfonic acid anion, higher alkylbenzenesulfonic acid anions such as p-dodecylbenzenesulfonic acid anion, higher alkyl sulfate anions such as lauryl sulfate anion, boric acid derivative anions such as tetraphenylboron, dialkylsulfosuccinate anions such as di-2-ethylhexylsulfosuccinate anion, polyether alcohol sulfate anions such as cetyl polyethenoxy sulfate anion, higher aliphatic anions such as stearic acid anion and polymers with an acid radical such as polyacrylic acid anion.

Examples of the compound represented by Formula I are given in Table.

Table

Compound No.	R_1	R_2	R_3	$X^{\ominus}$
I - 1	H	H	H	$C\ell^{\ominus}$
I - 2	H	p-CH_3	p-CH_3	$C\ell^{\ominus}$
I - 3	H	m-CH_3	m-CH_3	$C\ell^{\ominus}$
I - 4	H	o-CH_3	o-CH_3	$C\ell^{\ominus}$
I - 5	p-CH_3	p-CH_3	p-CH_3	$C\ell^{\ominus}$
I - 6	H	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
I - 7	H	m-OCH_3	m-OCH_3	$C\ell^{\ominus}$
I - 8	H	o-OCH_3	o-OCH_3	$C\ell^{\ominus}$
I - 9	p-OCH_3	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
I - 10	H	p-C_2H_5	p-C_2H_5	$C\ell^{\ominus}$
I - 11	H	m-C_2H_5	m-C_2H_5	$C\ell^{\ominus}$
I - 12	H	p-C_3H_7	p-C_3H_7	$C\ell^{\ominus}$
I - 13	H	p-OC_2H_5	p-OC_2H_5	$C\ell^{\ominus}$
I - 14	H	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
I - 15	H	p-OCH_3	p-OC_2H_5	$C\ell^{\ominus}$
I - 16	H	p-OC_5H_{11}	p-OCH_3	$C\ell^{\ominus}$
I - 17	H	p-OC_8H_{17}-n	p-OC_8H_{17}-n	$C\ell^{\ominus}$
I - 18	H	p-$C_{12}H_{25}$-n	p-$C_{12}H_{25}$-n	$C\ell^{\ominus}$
I - 19	H	p-$N(CH_3)_2$	p-$N(CH_3)_2$	$C\ell^{\ominus}$
I - 20	H	p-NH_2	p-NH_2	$C\ell^{\ominus}$
I - 21	H	p-OH	p-OH	$C\ell^{\ominus}$
I - 22	H	m-OH	m-OH	$C\ell^{\ominus}$
I - 23	H	p-$C\ell$	p-$C\ell$	$C\ell^{\ominus}$
I - 24	H	m-$C\ell$	m-$C\ell$	$C\ell^{\ominus}$
I - 25	p-CN	p-CH_3	p-CH_3	$C\ell^{\ominus}$
I - 26	p-SH	p-OCH_3	p-OCH_3	$C\ell^{\ominus}$
I - 27	H	p-OCH_3	p-OCH_3	

The tetrazolium compound can easily be synthesized in accordance with, for example, the method described in Chemical Reviews, vol. 55, pp. 335-483.

The tetrazolium compound represented by Formula I is used in the range of from about 1 mg to about 10 g, preferably about 10 mg to about 2 g, per mol silver halide contained in the silver halide photographic light-sensitive material of the present invention.

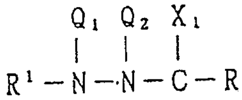
The tetrazolium compound represented by Formula I for the light-sensitive material of the present invention may be used singly or in combination of two or more kinds in appropriate ratios. It may also be used in combination with a tetrazolium compound in other than the compound of Formula I an appropriate ratio.

To obtain favolable result, an anion is preferably used with the tetrazolium compound, which is capable of binding with the tetrazolium compound so as to reduce the hydrophilicity of the tetrazolium compound. Examples of such anions include acid radicals of inorganic acids such as perchloric acid; acid radicals of organic acids such as sulfonic acid and carboxylic acid; and anionic surfactants, specifically lower alkylbenzenesulfonic acid anions such as p-toluenesulfonic acid anion, p-dodecylbenzenesulfonic acid anion, alkylnaphthalenesulfonic acid anions, lauryl sulfate anions, tetraphenylboron, dialkylsulfosuccinate anions such as di-2-ethylhexylsulfosuccinate anion, polyether alcohol sulfate anions such as cetyl polyethenoxysulfate anion, stearic acid anion and polyacrylic acid anion.

These anions may be added to the hydrophilic colloidal layer after mixed with the tetrazolium compound and may also be added singly to a silver halide emulsion layer or hydrophilic colloidal layer containing or not containing the tetrazolium compound.

The hydrazine compound preferably used in the light-sensitive material of the present invention is represented by the following formula II.

Formula II



$$R^1-\overset{\overset{\displaystyle Q_1}{|}}{N}-\overset{\overset{\displaystyle Q_2}{|}}{N}-\overset{\overset{\displaystyle X_1}{|}}{C}-R^2$$

wherein R^1 represents a monovalent organic group; R^2 represents a hydrogen atom or a monovalent organic group; Q_1 and Q_2 independently represent a hydrogen atom, an alkylsulfonyl group including those having a substituent or an arylsulfonyl group (including those having a substituent); X_1 represents an oxygen atom or a sulfur atom. Of the compounds represented by Formula II, those having an oxygen atom for X_1 and a hydrogen atom for R^2 are still more preferable.

The monovalent organic residue for R^1 and R^2 described above includes aromatic groups, heterocyclic residues and aliphatic groups.

The aromatic groups include a phenyl group, a naphthyl group and phenyl or naphthyl groups having a substituent such as alkyl group, alkoxy group, acylhydrazino group, dialkylamino group, alkoxycarbonyl group, cyano group, carboxy group, nitro group, alkylthio group, hydroxy group, sulfonyl group, carbamoyl group, halogen atom, acylamino group, sulfonamido group and thiourea group. Examples of those having a substituent include a 4-methylphenyl group, a 4-ethylphenyl group, a 4-oxyethylphenyl group, a 4-dodecylphenyl group, a 4-carboxyphenyl group, a 4-diethylaminophenyl group, a 4-octylaminophenyl group, a 4-benzylaminophenyl group, a 4-acetamido-2-methylphenyl group, a 4-(3-ethylthioureido)phenyl group, a 4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl group, a 4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl group.

The heterocyclic group is a 5- or 6-membered simple or condensed ring having at least one of an oxygen atom, a nitrogen atom, a sulfur atom and a selenium atom, and may have a substituent. Examples of the heterocyclic group include residues of a pyrroline ring, a pyridine ring, a quinoline ring, an indole ring, an oxazole ring, a benzoxazole ring, a naphthoxazole ring, an imidazole ring, a benzimidazole ring, a thiazoline ring, a thiazole ring, a benzothiazole ring, a naphthothiazole ring, a selenazole ring, a benzoselenazole ring and a naphthoselenazole ring.

These heterocyclic rings may be substituted by an alkyl group having 1 to 4 carbon atoms such as a methyl group or an ethyl group; an alkoxy group having 1 to 4 carbon atoms such as a methoxy group or an ethoxy group; an aryl group having a carbon number of 6 to 18 such as a phenyl group; a halogen atom such as chlorine or bromine; an alkoxycarbonyl group; a cyano group; an amino group.

Examples of the aliphatic group include normal and branched alkyl groups and cycloalkyl groups as well as those having a substituent, and alkenyl groups and alkynyl groups.

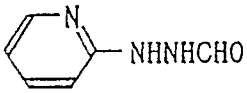
Examples of the normal and branched alkyl groups include those having 1 to 18 carbon atoms, preferably 1 to 8, such as a methyl group, an ethyl group, an isobutyl group and a 1-octyl group.

Examples of the cycloalkyl groups include those having 3 to 10 carbon atoms, such as a cyclopropyl group, a cyclohexyl group and an adamantyl group. Examples of the substituent for the alkyl group or cycloalkyl group include alkoxy groups such as methoxy group, ethoxy group, propoxy group and butoxy group, an alkoxycarbonyl group, a carbamoyl group, a hydroxy group, an alkylthio group, an amido group, an acyloxy group, a cyano group, a sulfonyl group, halogen atoms such as chlorine bronine flurorine and iodine atom, aryl group such as phenyl group, halogen-substituted phenyl group and alkyl-substituted phenyl group. Examples of substituted ones include a 3-methoxypropyl group, an ethoxycarbonylmethyl group, 4-chlorocyclohexyl group, a benzyl group, a p-methylbenzyl group and a p-chlorobenzyl group. Examples of the alkenyl group include an allyl group. Examples of the alkynyl group include a propargyl group.

Examples of preferable hydrazine compounds of the present invention are given below:

II-1: 1-formyl-2-{4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine
II-2: 1-formyl-2-(4-diethylaminophenyl)hydrazine
II-3: 1-formyl-2-(p-tolyl)hydrazine
II-4: 1-formyl-2-(4-ethylphenyl)hydrazine
II-5: 1-formyl-2-(4-acetamido-2-methylphenyl)hydrazine
II-6: 1-formyl-2-(4-oxyethylphenyl)hydrazine
II-7: 1-formyl-2-(4-N,N-dihydroxyethylaminophenyl)hydrazine
II-8: 1-formyl-2-[4-(3-ethylthioureido)phenyl)hydrazine
II-9: 1-thioformyl-2-{4-[2-(2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine
II-10: 1-formyl-2-(4-benzylaminophenyl)hydrazine
II-11: 1-formyl-2-(4-octylaminophenyl)hydrazine
II-12: 1-formyl-2-(4-dodecylphenyl)hydrazine
II-13: 1-acetyl-2-{4-2-2,4-di-tert-butylphenoxy)butylamido]phenyl}hydrazine
II-14: 4-carboxyphenylhydrazine
II-15: 1-acetyl-1-(4-methylphenylsulfonyl)-2-phenylhydrazine
II-16: 1-ethoxycarbonyl-1-(4-methylphenylsulfonyl)-2-phenylhydrazine
II-17: 1-formyl-2-(4-hydroxyphenyl)-2-(4-methylphenylsulfonyl)-phenylhydrazine
II-18: 1-(4-acetoxyphenyl)-2-formyl-1-(4-methylphenylsulfonyl)-phenylhydrazine
II-19: 1-formyl-2-(4-hexanoxyphenyl)-2-(4-methylphenylsulfonyl)-hydrazine
II-20: 1-formyl-2-[4-(tetrahydro-2H-pyran-2-yloxy)phenyl]-2-(4-methylphenylsulfonyl)-hydrazine
II-21: 1-formyl-2-[4-(3-hexylureidophenyl)]-2-(4-methylphenylsulfonyl)-hydrazine
II-22: 1-formyl-2-(4-methylphenylsulfonyl)-2-[4-(phenoxythiocarbonylamino)-phenyl]-hydrazine
II-23: 1-(4-ethoxythiocarbonylaminophenyl)-2-formyl-1-(4-methylphenylsulfonyl)-hydrazine
II-24: 1-formyl-2-(4-methylphenylsulfonyl)-2-[4-(3-methyl-3-phenyl-2-thioureido)-phenyl]-hydrazine
II-25: {{1-{4-{3-[4[(2,4-bis-t-amylphenoxy)-butyl]-ureido}-phenyl}}-2-formyl-1-(4-methylphenylsulfonyl)-hydrazine

II - 26



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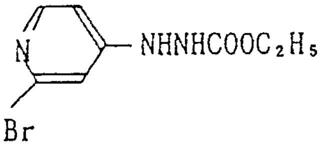

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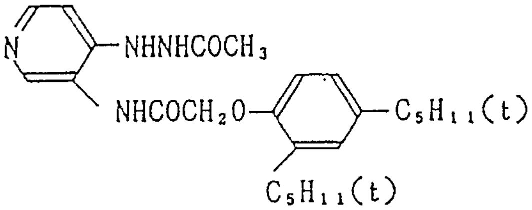

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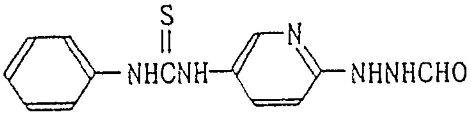

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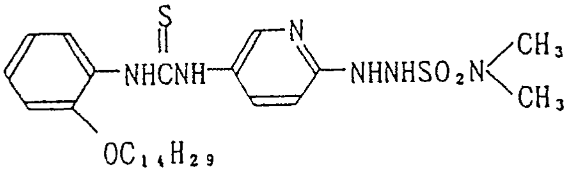

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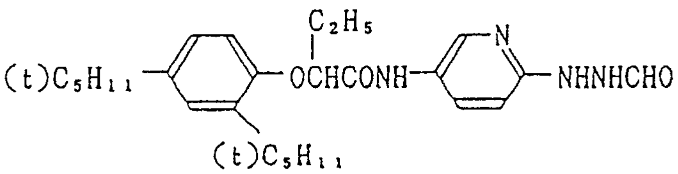

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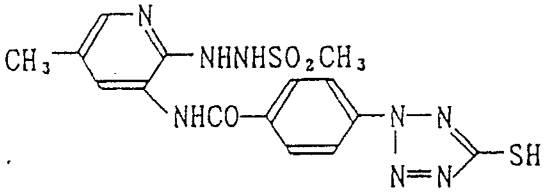

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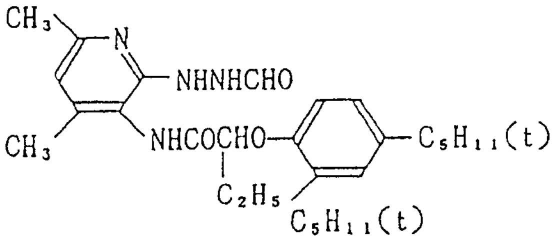

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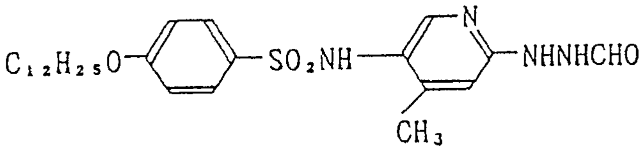

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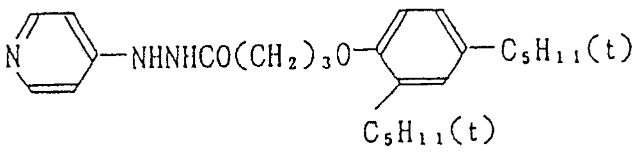

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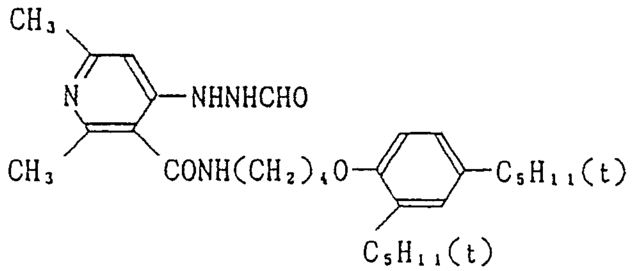

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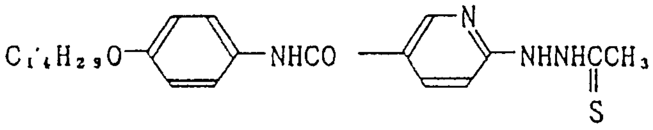

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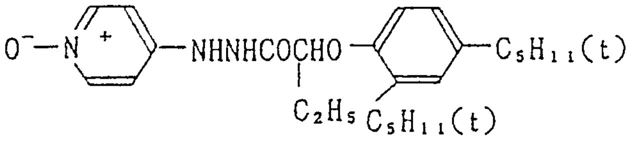

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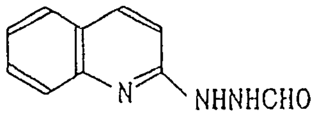

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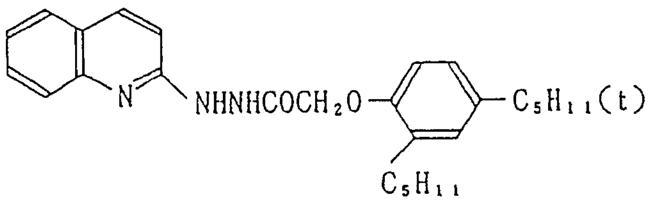

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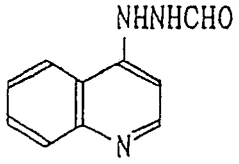

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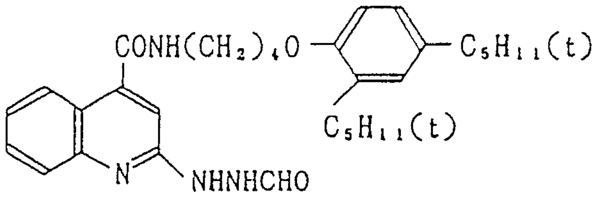

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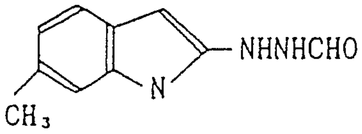

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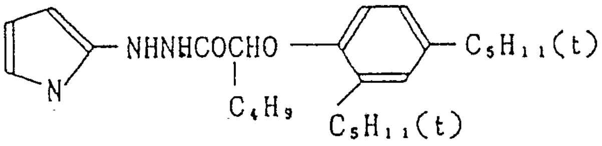

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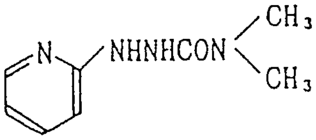

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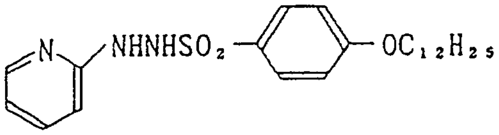

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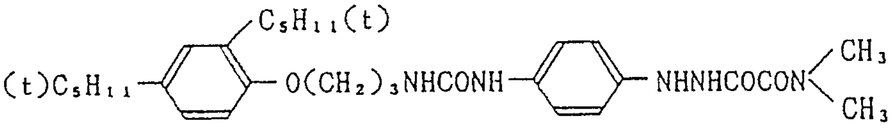

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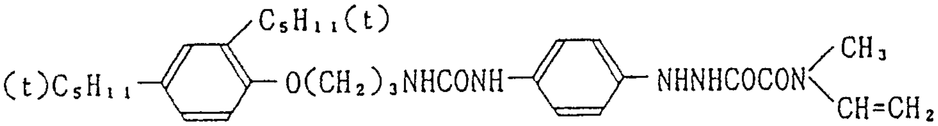

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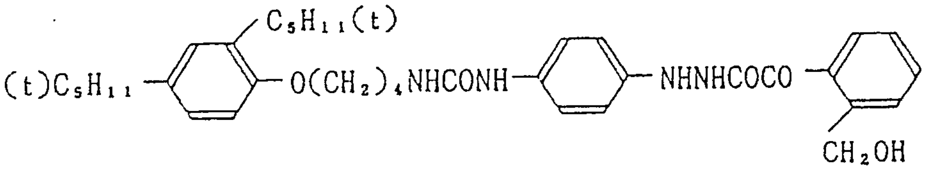

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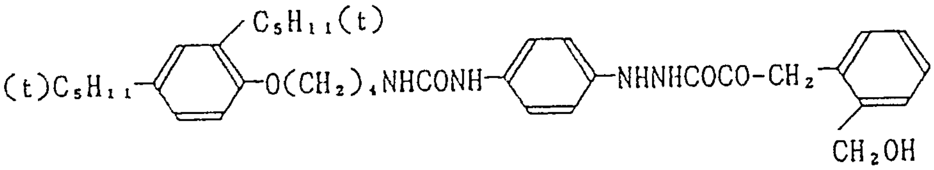

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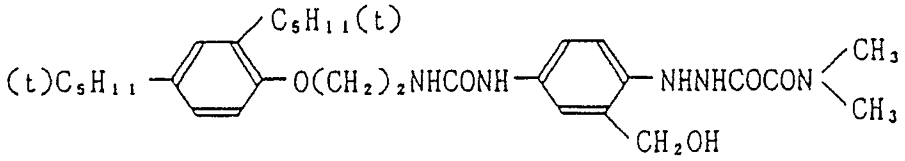

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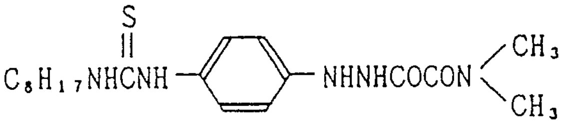

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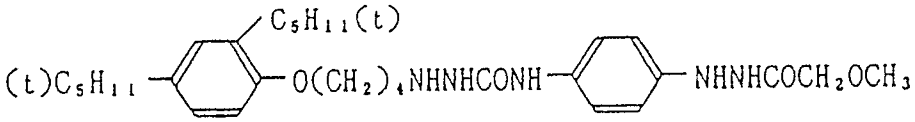

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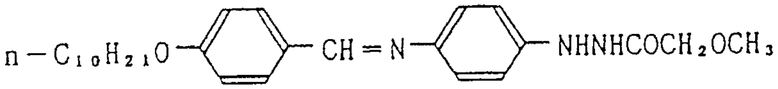

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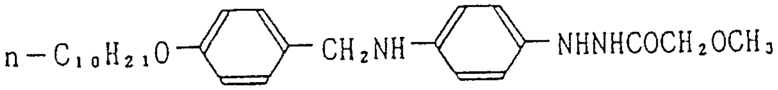

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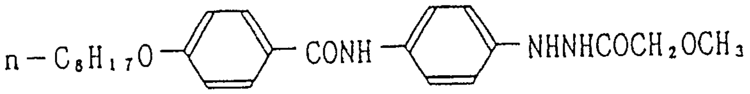

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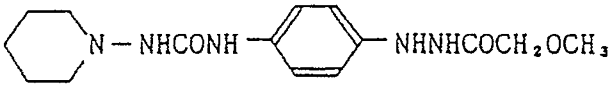

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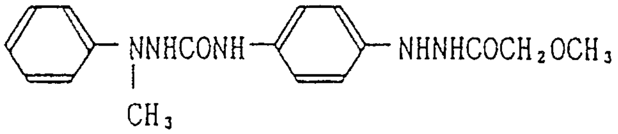

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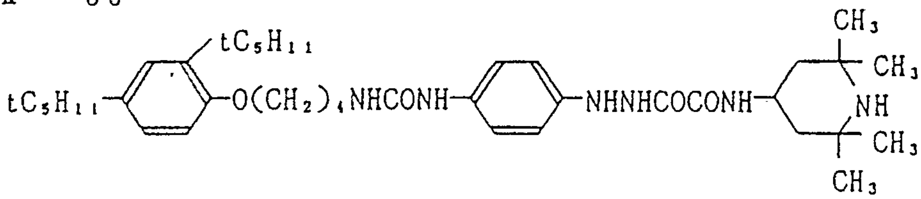


The hydrazine compound represented by Formula II is added to the silver halide emulsion layer and/or a non-light-sensitive layer located on the silver halide emulsion layer side of the support, preferably to the silver halide emulsion layer and/or a layer located thereunder. The amount preferable of addition of the hydrazine compound is 10^{-5} to 10^{-1} mol/mol silver, more preferably 10^{-4} to 10^{-2} mol/mol silver contained in the emulsion layer.

Any silver halide used in ordinary silver halide emulsions, such as silver bromide, silver iodobromide, silver chloride, silver chlorobromide and silver chloroiodobromide can be used in the silver halide emulsion for the light-sensitive material of the present invention, with preference given to a negative type silver chlorobromide emulsion containing not less than 50 mol% silver chloride. The silver halide grains may be prepared by any of the acid process, the neutral process and the ammonia process. The silver halide emulsion for the present invention may be comprised of a single composition or number of different compositions which may contain in a single layer or in a number of layers separately.

Any shape can be used for the silver halide grains of the present invention. An example of preferable shape is a cube having a [100] face as a crystalline surface. It is also possible to prepare octahedral, tetradecahedral or dodecahedral grains by the methods described in references such as US Patent Nos. 4,183,756 and 4,225,666, Japanese Patent Publication Open to Public Inspection No. 26589/1980, Japanese Patent Examined Publication No. 42737/1980 and the Journal of Photographic Science, 21, 39 (1973) and use them. It is also possible to use grains having a twin face.

The silver halide grains of the present invention may be in a single shape or comprise a number of different forms.

Any grain size distribution is acceptable. It is possible to use an emulsion with a wide grain size distribution, referred to as a polydisperse emulsion, and to use an emulsion with a narrow grain size distribution, referred to as a monodisperse emulsion, singly or in combination. A polydisperse emulsion and a monodisperse emulsion may be used in combination.

Two or more separately prepared silver halide emulsions may be used in combination.

For the present invention, it is preferable to use a monodisperse emulsion.

The highly monodisperse emulsion preferably has a grain size distribution width of not more than 20%, more preferably not more than 15%, as defined by the following equation:

$$\frac{\text{(Standard deviation of grain size}}{\text{Average grain size } \bar{r})} \times 100 = \text{distribution width (\%)}$$

Here, average grain size r is defined as the grain size $\bar{r}$ that gives the maximum value of ni x ri^3, the product of ni = frequency of grains having a grain size of ri and ri^3. (Three digits are significant, with the last digit figure rounded off.)

When a spherical silver halide grain is concerned, grain size means its diameter. When a non-spherical silver halide grain is concerned, grain size means the diameter of the circular image converted from its projection with the same area.

Grain size can be determined by, for example, taking an electron micrograph of the subject grain at a magnifying rate of 10000 to 50000 and measuring the diameter of the printed grain image or the area of the projected image. Randomly not less than 1000 grains should be involved in the measurement.

A monodisperse emulsion can be obtained in accordance with, for example, Japanese Patent Publication Open to Public Inspection Nos. 48521/1979, 49938/1983 and 122935/1985.

The light-sensitive silver halide emulsion can be used in the form of a primitive emulsion without chemical sensitization, but is normally used after chemical sensitization.

Chemical sensitization can be carried out by the methods described in the above-mentioned books written by Glafkides or Zelikman et al. and the method described in Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden, Akademische Verlagsgesellschaft, edited by H. Frieser (1968).

Accordingly, it is possible to use singly or in combination sulfur sensitization with a compound containing sulfur reactable with silver ion or an active gelating, reduction sensitization with a reducing agent, and noble metal sensitization using gold or another noble metal compound. Thiosulfates, thioureas, thiazoles, rhodanines and other compounds can be used as sulfur sensitizers. Examples of these sensitizers are described in US Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668 and 3,656,955. Stannous salts, amines, hydrazine derivatives, formamidinosulfinic acid, silane compounds, etc. can be used as reduction sensitizers. Examples of these sensitizers are described in US Patent Nos. 2,487,850, 2,419,974, 2,518,698, 2,983,609, 2,983,610 and 2,694,637. For noble metal sensitization, complex salts of metals listed under Group VII in the periodic table such as platinum, iridium and palladium, as well as gold complex salts, can be used. Examples of these sensitizers are described in US Patent Nos. 2,399,083 and 2,448,060 and British Patent No. 618,061.

Although there is no particular limitation on a chemical sensitization condition such as pH, pAg or temperature, it is preferable to maintain a pH value of 4 to 9, more preferably 5 to 8, a pAg value of 5 to 11, more preferably 8 to 10, and a temperature of 40 to 90° C, more preferably 45 to 75° C.

With respect to the light-sensitive emulsion, the emulsions described above may be used singly or in combination.

In the embodiment of the present invention, various stabilizers such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 5-mercapto-1-phenyltetrazole and 2-mercaprobenzothiazole can be used after completion of the chemical sensitization described above. Also, silver halide solvents such as thioether and crystal habit controlling agents such as mercapto-containing compounds and sensitizing dyes may be used as desired.

The silver halide grains used for the emulsion may have metal ions, inside and/or surface of them, as added using a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or complex, a rhodium salt or complex or an iron salt or complex during formation and/or growth of the grains.

After completion of silver halide grain growth, the unnecessary soluble salts may be removed from the emulsion, or may remain contained therein. These salts can be removed in accordance with the method described in Research Disclosure No. 17643.

The photographic emulsion used in the silver halide photographic light-sensitive material of the present invention may be spectrally sensitized with a sensitizing dye for blue light of relatively long wavelength, green light, red light or infrared light. Examples of usable dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Cyanine dyes, merocyanine dyes and complex merocyanine dyes are particularly useful. To these dyes, any nucleus which is normally utilized in cyanine dyes as basic heterocyclic nucleus is applicable. Examples of applicable nuclei include a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus and a pyridine nucleus; a nuclei resulting from condensation of these nuclei with an alicyclic hydrocarbon ring and those resulting from condensation of these nuclei with an aromatic hydrocarbon ring such as an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzotiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus. These nuclei may have a substituent at a carbon atom thereof.

As the nucleus having a ketomethylene structure of the merocyanine dye or complex merocyanine dye such a 5- or 6-membered heterocyclic nucleus such as a pyrrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus and a thiobarbituric acid nucleus may be applicable.

The sensitizing dye for the present invention is used at similar concentrations to those used for ordinary negative silver halide emulsions. It is advantageous to use it at a dye concentration at which the specific sensitivity of the silver halide emulsion is not substantially degraded. It is preferable to use the sensitizing dye in an amount of about 1.0 x 10^{-5} to about 5 x 10^{-4} mol, more preferably about 4 x 10^{-5} to 2 x 10^{-4} mol, per mol silver halide.

The sensitizing dye can be used singly or in combination of some kinds. More specifically, the following sensitizing dyes can serve well for the present invention.

Examples of sensitizing dyes used in the blue-sensitive silver halide emulsion layer include those described in West German Patent No. 929,080, US Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,956, 3,672,897, 3,694,217, 4,025,349 and 4,046,572, British Patent No. 1,242,588, Japanese Patent Examined Publication Nos. 14030/1969 and 24844/1977 and Japanese Patent Publication Open to Public Inspection Nos. 73137/1973 and 172140/1986. Typical examples of sensitizing dyes used in the green-sensitive silver halide emulsion layer include the cyanine dyes, merocyanine dyes or complex merocyanine dyes described in US Patent Nos. 1,939,201, 2,072,908, 2,739,149 and 2,945,763, British Patent No. 505,979 and Japanese Patent Examined Publication No. 42172/1973. Typical examples of sensitizing dyes used in the red- and infrared-sensitive silver halide emulsion layers include the cyanine dyes, merocyanine dyes or complex merocyanine dyes described in US Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629 and 2,776,280, Japanese Patent Examined Publication No. 17725/1974 and Japanese Patent Publication Open to Public Inspection Nos. 62425/1975, 29836/1986 and 80841/1985.

These sensitizing dyes may be used singly or in combination. Sensitizing dyes are often combined together for the purpose of supersensitization. Typical examples thereof are given in US Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, British Patent Nos. 1,344,281 and 1,507,803, Japanese Patent Examined Publication Nos. 4936/1968 and 12375/1978 and Japanese Patent Publication Open to Public Inspection Nos. 110618/1977 and 109925/1977.

When the hydrophilic colloidal layer of the silver halide photographic light-sensitive material of the present invention contains a dye, an ultraviolet absorbent, they may be mordanted with a mordant such as a cationic polymer. The photographic emulsion described above may contain various compounds as known as stabilizers to prevent sensitivity reduction and fogging during preparation, storage or processing of the silver halide photographic light-sensitive material. As the stabilizers, it is possible to add azoles such as benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles and benzimidazoles, particularly nitro- or halogen-substitution products thereof; heterocyclic mercapto compounds such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles and mercaptotetrazoles, particularly 1-phenyl-5-mercaptotetrazole, mercaptopyridines, the above-mentioned heterocycles having a water-solubilizing group such as a carboxyl group or a sulfono group; mercapto compounds; thioketo compounds such as oxazolinethione; azaindenes such as tetrazaindenes particularly 4-hydroxy-substituted (1,3,3a,7)-tetrazaindenes; and benzenethiosulfonic acids and benzenesulfinic acids.

Examples of usable compounds are listed by K. Mees in the Theory of the Photographic Process, 3rd edition (1966) with mention of original references.

More specific examples thereof and methods of their use are described in, for example, US Patent Nos. 3,954,474, 3,982,947 and 4,021,248 and Japanese Patent Examined Publication No. 28660/1977.

The silver halide photographic light-sensitive material of the present invention may contain the following additives. Examples of thickeners or plasticizers include the substances described in US Patent No. 2,960,404, Japanese Patent Examined Publication No. 4939/1968, West German DAS Patent No. 1,904,604, Japanese Patent Publication Open to Public Inspection No. 63715/1973, Japanese Patent Examined Publication No.15462/1970, Belgian Patent No. 762,833, US Patent No. 3,767,410 and Belgian Patent No. 558,143, such as styrene-sodium maleate copolymers and dextran sulfate. Examples of hardeners include aldehyde-type, epoxy-type, ethyleneimine-type, active halogen-type, vinylsulfone-type, isocyanate-type, sulfonate-type, carbodiimide-type, mucochloric acid-type and acyloyl-type hardeners. Examples of ultraviolet absorbents include the compounds described in US Patent No. 3,253,921 and British Patent No.

1,309,349, particularly 2-(2′-hydroxy-5-tert-butylphenyl)benzotriazole, 2-(2′-hydroxy-3′-5′-di-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-3′-tert-butyl-5′-butylphenyl)-5-chlorobenzotriazole and 2-(2′-hydroxy-3′-5′-di-tert-butylphenyl)-5-chlorobenzotriazole. In the light sensitive material, surfactants may be used as coating aids, emulsifiers, processing solution permeability improvers, deforming agents. For such purposes the anionic, cationic, nonionic or amphoteric compounds may be used, which are described in British Patent Nos. 548,532 and 1,216,389, US Patent Nos. 2,026,202 and 3,514,293, Japanese Patent Examined Publication Nos. 26580/1969, 17922/1968, 17926/1968, 13166/1968 and 20785/1973, French Patent No. 202,588, Belgian Patent No. 773,459 and Japanese Patent Publication Open to Public Inspection No. 101118/1973. Of these surfactants, anionic surfactants having a sulfone group, such as succinate sulfonates, alkylnaphthalenesulfonates and alkylbenzenesulfonates are preferable.

In the production process of the light-sensitive material it is preferable that the pH of the coating solution is in the range of from 5.3 to 7.5. In the case of multiple layer coating, it is preferable that the pH of the mixture prepared by mixing the coating solutions for respective layers in the same ratio as the coating amount ratio is in the above-mentioned range of from 5.3 to 7.5. pH values lower than 5.3 causes too slow hardening speed of the coated layer, and pH value higher than 7.5 causes undesirable effects on photographic properties of the light-sensitive material.

The structural layer of the light-sensitive material of the present invention may contain a lubricant such as the higher alcohol esters of higher fatty acids described in US Patent Nos. 2,588,756 and 3,121,060, the casein described in US Patent No. 3,295,979, the higher fatty acid calcium salt described in British Patent No. 1,263,722 and the silicon compounds described in British Patent No. 1,313,384 and US Patent Nos. 3,042,522 and 3,489,567. Dispersion of liquid paraffin can also be used for this purpose.

Examples of brightening agents which can serve well include stilbene-type, triazine-type, pyrazoline-type, coumarin-type and acetylene-type brightening agents.

These compounds may be used in aqueous solution or, if they are insoluble in water, may be used in dispersion.

Examples of preferable anionic surfaotants include those having an acidic group such as a carboxy group, a sulfo group, a phospho group, a sulfate group or a phosphate group, for example, alkyl carboxylates, alkyl sulfonates, alkyl benzenesulfonates, alkyl naphthalenesulfonates, alkyl sulfates, alkyl phosphates, N-acyl-alkyltaurins, sulfosuccinates, sulfoalkylpolyoxyethylenealkylphenyl ethers and polyoxyethylenealkyl phosphates.

Examples of preferable amphoteric surfactants include amino acids, aminoalkylsulfonic acids, aminoalkylsulfates or phosphates, alkylbetaines and amine oxides.

Examples of preferable cationic surfactants include alkylamine salts, aliphatic or aromatic quaternary ammonium salts, quaternary ammonium salts of heterocycles such as pyridinium and imidazolium, and aliphatic phosphonium or sulfonium salts and phosphonium or sulfonium salts containing a heterocyclic ring.

Examples of preferable nonionic surfactants include steroids such as saponin, alkylene oxide derivatives such as polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, polyethylene oxide adducts of silicone, glycide derivatives such as alkenyl succinic polyglyceride, alkylphenol polyglyceride, polyhydric alcohol fatty acid esters and sugar alkyl esters.

It is also possible to use the technique wherein a polymer latex is added to the silver halide emulsion layer or backing layer to improve dimensional stability. Specific procedures of this art are described in, for example, Japanese Patent Examined Publication Nos. 4272/1964, 17702/1964 and 13482/1968, US Patent Nos. 2,376,005, 2,763,625, 2,772,166, 2,852,386, 2,853,457 and 3,397,988.

Gelatin is used as a binder for the light-sensitive material for the present invention, but it can be used in combination with hydrophilic colloids such as gelatin derivatives, cellulose derivatives, graft polymers comprising gelatin and another polymer, other proteins, sugar derivatives, cellulose derivatives, and synthetic hydrophilic or copolymers.

In addition to lime-treated gelatin, acid-treated gelatin and oxygen-treated gelatin described in Bulletin of Society of Photographic Sooiety of Japan, No. 16, p. 30 (1966) may be used. It is also possible to use hydrolyzates and enzymolyzates of gelatin. The gelatin derivatives used are those obtained by reacting gelatin with various compounds such as acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkane sultones, vinylsulfonamides, maleic imide compounds, polyalkylene oxides and epoxy compounds. Examples thereof are given in, for example, US Patent Nos. 2,614,928, 3,132,945, 3,186,846 and 3,312,553, British Patent Nos. 861,414, 1,033,189 and 1,005,784 and Japanese Patent Examined Publication No. 26845/1966.

Substances usable in combination with gelatin are albumin and casein of proteins, hydroxyethylcellulose, carboxymethylcellulose and cellulose sulfate of cellulose derivatives and sodium arginate and starch derivatives of sugar derivatives.

The graft polymer of gelatin and another polymer described above is prepared by grafting gelatin with acrylic acid, methacrylic acid, there derivatives such as esters and amides thereof, a homo or copolymer of a vinyl monomer such as acrylonitrile or styrene, with particular preference given to a graft polymer with a polymer showing some compatibility with gelatin, such as a polymer of acrylic acid, acrylamide, methacrylamide or hydroxyalkyl methacrylate. Specific examples thereof are given in, for example, US Patent Nos. 2,763,625, 2,831,767 and 2,956,884.

The light-sensitive material of the present invention may contain various additives as desired. These additives are more specifically described in Research Disclosures, vol. 176, Item 17643 (December 1978) and vol. 187, Item 18716 (November 1979). In the following table are listed the portions where these additives are described in detail.

	Type of additive	RD17643	RD18716
1.	Chemical sensitizer	p. 23	p. 648 right column
2.	Sensitivity increasing agent		Ditto
3.	Spectral sensitizer/supersensitizer	pp. 23-24	p. 648 right column to p. 649 right column
4.	Brightening agent	p. 24	
5.	Antifogging agent/stabilizer	p. 24-25	p. 649 right column
6.	Light absorbent/filter dye/ultraviolet absorbent	p. 25-26	p. 649 right column to p. 650 left column
7.	Antistaining agent	p. 25 right column	p. 650 left column to right column
8.	Dye image stabilizer	p. 25	
9.	Hardener	p. 26	p. 651 left column
10.	Binder	p. 26	p. 651 left column
11.	Plasticizer/lubricant	p. 27	p. 650 right column
12.	Coating aid/surfactant	p. 26-27	Ditto
13.	Antistatic agent	p. 27	Ditto

The support used for the light-sensitive material of the present invention includes flexible reflective supports such as paper laminated with -olefin polymer such as polyethylene, polypropylene, ethylene/butene copolymer, and synthetic paper; films comprising semi-synthetic or synthetic polymer such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate or polyamide; flexible supports prepared by forming a reflective layer on these films; and metals. Polyethylene terephthalate is particularly preferable.

Examples of subbing layers usable for the present invention include the subbing layers prepared with an organic solvent system containing a polyhydroxybenzene described in Japanese Patent Publication Open to Public Inspection No. 3972/1974 and the aqueous latex subbing layers described in Japanese Patent Publication Open to Public Inspection Nos. 11118/1974, 104913/1977, 19941/1984, 19940/1984, 18945/1984, 112326/1976, 17617/1976, 58469/1976, 114120/1976, 121323/1976, 123139/1976, 114121/1976, 13932/1977, 65422/1977, 109923/1977, 119919/1977, 65949/1980, 128332/1982 and 19941/1984.

The subbing layer may usually be subjected to chemical or physical surface treatment. Examples of the treatment include surface activating treatments such as chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet treatment, microwave treatment, glow discharge treatment, active plasma treatment, laser treatment, mixed acid treatment and ozonization treatment.

The subbing layer is differentiated from the coated layer of the present invention, and there is no limitation on the coating timing or conditions.

In the present invention, filter dyes and other dyes can be used for the prevention of halation and other purposes. Examples of usable dyes include triallyl dyes, oxanol dyes, hemioxanol dyes, merocyanine dyes, cyanine dyes, styryl dyes and azo dyes. Of these dyes, oxanol dyes, hemioxanol dyes and merocyanine dyes are particularly useful. Examples of usable dyes are given in, for example, West Germany Patent Nos. 616,007, British Patent Nos. 584,609 and 1,177,429, Japanese Patent Examined Publication Nos.

7777/1951, 22069/1964 and 38129/1979, Japanese Patent Publication Open to Public Inspection Nos. 85130/1973, 99620/19704 114420/1974, 129537/1974, 28827/1975, 108115/1977, 185038/1982 and 24845/1984, US Patent Nos. 1,878,961, 1,884,035, 1,912,797, 2,098,891, 2,150,695, 2,274,782, 2,298,731, 2,409,612, 2,461,484, 2,527,583, 2,533,472, 2,865,752, 2,956,879, 3,094,418, 3,125,448, 3,148,187, 3,177,078, 3,247,127, 3,260,601, 3,282,699, 3,409,433, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 3,865,817, 4,070,352 and 4,071,312, PB Report No. 74175 and Photographic Abstract 1 , 28 ('21).

Use of these dyes is preferable for a contact printing light-sensitive material for handling under room light, with particular preference given to use to allow the sensitivity to light at 400 nm is not less than 30 times that to light at 360 nm.

In the embodiment of the present invention, the organic desensitizer wherein the sum of the polarographic cathode potential and anode potential has a positive value described in Japanese Patent Publication Open to Public Inspection No. 26041/1986 can be used.

The light-sensitive material of the present invention can be exposed using an electromagnetic wave in the spectral region where the emulsicn layer of the light-sensitive material has a sensitivity. Any light source can be used, such as natural light, e.g. solar ray, tungsten lamp, fluorescent lamp, iodine quartz lamp, mercury lamp, microwave luminescent UV lamp, xenone arc lamp, carbon arc lamp, xenone flash lamp, flying spot of cathode ray tube, various laser beams, luminescent diode light and light emitted from a phosphor excited by electron beams, X ray, γ ray, or α ray. Favorable results can be obtained when an UV light source described in Japanese Patent Publication Open to Public Inspection No. 2104581/1987 equipped with filter that absorbs light at a wavelength of not more than 370 nm or an UV light having a main wavelength at 370 to 420 nm is used as a light source.

Exposure time may be shorter than 1 microsecond, as well as between 1 millisecond and 1 second, the range normally used for cameras. For example, an exposure time of 100 nanosecond to 1 microsecond is also possible, as obtained using a cathode ray tube or a xenone flush tube, and it may exceed 1 second. Exposure may be carried out continuously or intermittently.

The present invention is applicable to various light-sensitive materials including graphic arts films, radiography films, ordinary negative films, ordinary reversal films, ordinary positive films and direct positive films, with a noticeable effect obtained when it is applied to light-sensitive materials for graphic arts use, where very high degree of dimensional stability is needed.

In the present invention, various developing processes can be used for processing the light-sensitive material, such as black-and-white, color and reversal development by a known method, with its effect enhanced in the processing of a light-sensitive material for graphic arts that provides a high contrast.

The fixer usable for the present invention may contain various acids, salts, fixation accelerators, wetting agents, surfactants, chelating agents, hardeners, etc., as well as thiosulfates and sulfites. Examples of thiosulfates and sulfites include potassium, sodium and ammonium salts of these acids. Examples of acids include sulfuric acid, hydrochloric acid, nitric acid, boric acid, formic acid, acetic acid, propionic acid, oxalic acid, tartaric acid, citric acid, malic and phthalic acid. Examples of salts include potassium, sodium and ammonium salts of these acids. Examples of fixation accelerators include the thiourea derivatives described in Japanese Patent Examined Publication No. 35754/1070 and Japanese Patent Publication Open to Public Inspection Nos. 122535/1983 and 122536/1983, alcohols having a triple bond in their molecular structure, the thioether described in US Patent No. 4,126,459, anion-releasing cyclodextran ether compounds, crown ethers, diazabicycloundecene and di(hydroxyethyl)butamine. Examples of wetting agents include alkanolamine and alkylen glycol. Examples of chelating agents include aminoacetic acids such as nitrilotriacetic acid and EDTA. Examples of hardeners include chromium alum, potassium alum and Aℓ compounds.

It is preferable that the fixer of the present invention contain an Aℓ compound to increase the degree of hardening of the light-sensitive material. It is still more preferable that its content be 0.1 to 3 g/ℓ as converted to the Aℓ content of the solution used.

The preferable sulfite concentration in the fixer is 0.03 to 0.4 mol/ℓ, more preferably 0.04 to 0.3 mol/ℓ.

The pH value of the fixer is preferably 3.9 to 6.5, more preferably 4.2 to 5.3.

It is preferable that the developing temperature for the silver halide photographic light-sensitive material of the present invention is not more than 50°C, with more preference given to the range of from 25 to 40°C. Development is generally completed within 2 minutes, but a favorable photographic image can be obtained even by quick processing in 5 to 25 seconds.

EXAMPLES

Example 1

A negative silver halide light-sensitive material for contact printing under roomlight was prepared as follows:

Preparation of emulsion

A silver chlorobromide emulsion having a silver bromide content of 2 mol% was prepared as follows:

An aqueous solution containing 23.9 mg, per 60 g silver nitrate, of potassium bromorhodate, sodium chloride and potassium bromide and another aqueous solution of silver nitrate were simultaneously added to an aqueous solution of gelatin with stirring at 40 °C for 25 minutes to prepare a silver chlorobromide emulsion having an average grain size of 0.20 µm.

After adding 200 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene as a stabilizer, this emulsion was washed and desalted.

The emulsion was subjected to sulfur sensitization after adding 20 mg of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene. A necessary amount of gelatin, and 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene, as a stabilizer, was added to the emulsion. Then, water was added to reach a final quantity of 260 mℓ to prepare a finished emulsion.

Preparation of latex (L) to be added to emulsion

KMDS (dextran sulfate sodium salt, produced by Meito Sangyo) of 0.25 kg and 0.05 kg of ammonium persulfate were added to 40ℓ of water. To this liquid, a mixture of 4.51 kg of n-butyl acrylate, 5.49 kg of styrene and 0.1 kg of acrylic acid was added at a liquid temperature of 81 °C with stirring in a nitrogen atmosphere over a period of 1 hour. Then, 0.005 kg of ammonium persulfate was added, followed by stirring for 1.5 hours. After cooling, this liquid was adjusted to a pH of 6 with aqueous ammonia.

The resulting latex liquid was filtered through a Whotman GF/D filter, and the resulting filtrate was diluted with water to reach a total weight of 50.5 kg to obtain a monodispersible latex (L) having an average grain size of 0.25µ.

Preparation of emulsion coating solution

To the emulsion described above, the following additives were added to yield a silver halide emulsion coating solution as follows:

After adding 9 mg of compound (A) as a fungicide, the emulsion described above was adjusted to a pH of 6.5 with a 0.5 N sodium hydroxide solution. Then, 360 mg of the following compound (T) was added, followed by sequential additions of 5 mℓ of a 20% aqueous solution of saponin, 180 mg of sodium dodecylbenzenesulfonate, 80 mg of 5-methylbenztriazole and 43 mℓ of the emulsion additive latex (L) described above, and then 60 mg of compound (M) and 280 mg of a styrene-maleic acid copolymer aqueous polymer as a thickener, per mol silver halide. Finally, water was added to reach a final quantity of 475 mℓ to prepare an emulsion coating solution.

Preparation of emulsion protective layer coating solutions

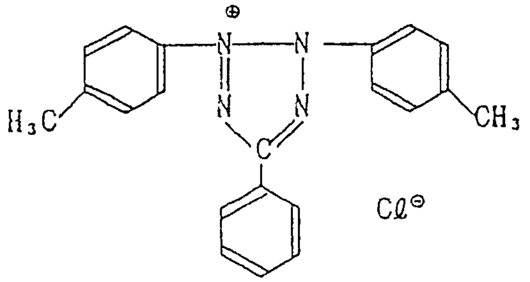
Next, emulsion protective film coating solutions were prepared as follows:

Pure water was added to gelatin. After swelling, the gelatin was dissolved, followed by sequential additions of a 1% aqueous solution of the following compound (Z) as a coating aid and the following compounds (N) and (B) as filter dyes. This mixture was adjusted to a pH of 6.0 with a citric acid solution. To this solution, matting agents comprising irregular-shaped silica particles were added at a rate shown in Table 1 to yield emulsion protective film coating solutions P-1 through P-8.

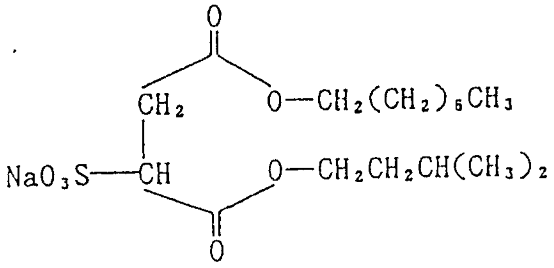
Table 1

	Matting agent A	Matting agent B	
P-1	20 mg/M^2	0 mg/m^2	Comparative
P-2	0	20	Comparative
P-3	10	4	Inventive
P-4	10	10	Inventive
P-5	10	20	Inventive
P-6	10	40	Inventive
P-7	4	20	Inventive
P-8	40	20	Inventive
Matting agent A: Average particle size: 3 µm (particles having a grain size exceeding 4 µm were removed by sieving) Matting agent B: Average particle size: 6 µm (grains having a grain size below 4 µm were removed by sieving)			

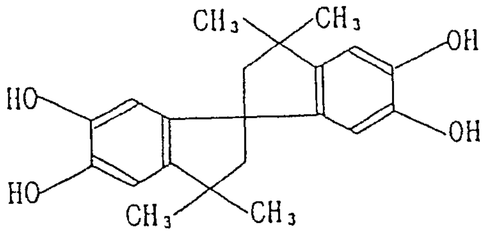
Compound (T)



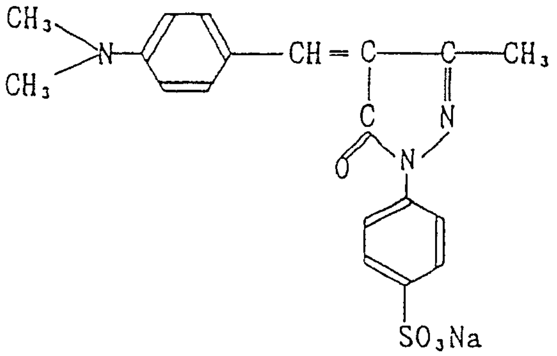
Compound (Z)



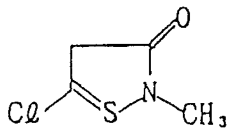
Compound (M)



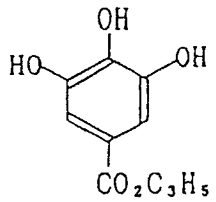
Compound (N)



Compound (A)



Compound (B)

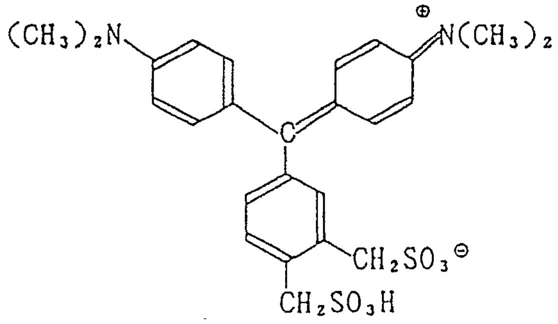


Preparation of backing coating solution B-1

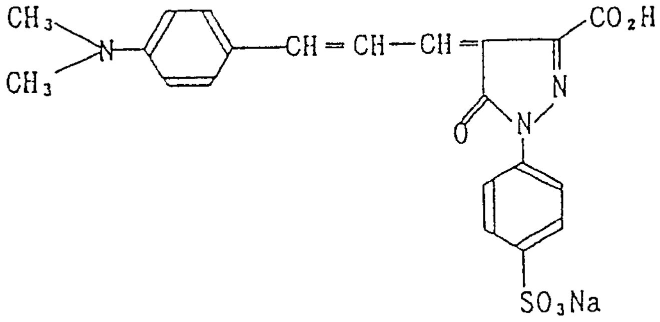
Next, a backing coating solution for a backing base layer was prepared as follows:

Gelatin of 36 g was swelled in water and dissolved therein with heating. To this solution, an aqueous solution of 1.6 g of the following compound (C-1), 310 mg of the following compound (C-2), 1.9 g of the following compound (C-3) and 2.9 g of the above-mentioned compound (N) were added as backing dyes. Then, 11 mℓ of a 20% aqueous solution of saponin and 5 g of the following compound (C-4) as a property regulator were added, followed by the addition of 63 mg of the following compound (C-5) in methanol solution. Viscosity was adjusted by the addition of 800 g of a water soluble polymer of a styrene-maleic acid copolymer as a thickener, and an aqueous solution of citric acid was added to obtain a pH of 5.4. Finally, 144 mg of glyoxal was added and water was added to reach a final quantity of 960 mℓ to obtain BC coating solution B-1.

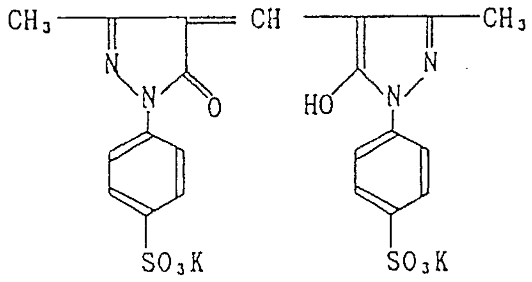
Compound (C-1)



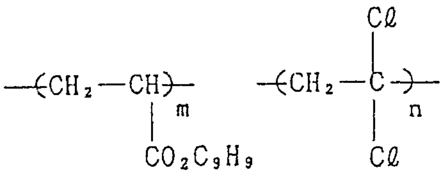
Compound (C-2)



Compound (C-3)



Compound (C-4)

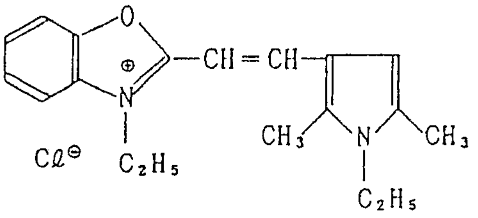


$$-\!\left(CH_2-\underset{CO_2C_9H_9}{CH}\right)_m\!- \qquad -\!\left(CH_2-\underset{Cl}{\overset{Cl}{C}}\right)_n\!-$$

Copolymer latex of

and wherein m:n = 1:1.

Compound (C-5)



Preparation of backing protective layer coating solutions B-2a and B-2b

Next, backing layer protective film coating solutions B-2a and B-2b were prepared as follows:

Gelatin of 50 g was swelled in water and dissolved therein with heating. To this solution, 340 mg of sodium salt of 2-sulfonate-succinic acid bis(2-ethylhexyl) ester, 3.4 g of sodium chloride, 1.1 g of glyoxal and 540 mg of mucochloric acid were added. To this mixture, spherical particles of polymethyl methacrylate having an average grain size of 4 µm were added as a matting agent at a final rate of 150 mg/m^2 or 40 mg/m^2. Water was added to reach a total quantity of 1000 mℓ to prepare protective layer coating solutions B-2a and B-2b.

Preparation of samples

Each of the coating solutions described above was coated on either side and then the other side of a subbed polyethylene terephthalate film having the thickness of 100 µm. In coating the emulsion layer side, the following two drying conditions were used.

Average surface temperature at a water content of 400%

Conditions A: 27° C (comparative)
Conditions B: 17° C (inventive)

A backing layer was formed on either side of the subbed support using coating solution B-1 to reach a dry weight of gelatin of 2 g/m^2. At the same time, a backing protective layer was formed on the backing layer using protective layer coating solutions B-2a or B-2b to reach a dry weight of gelatin of 1 g/m^2. Then, on the other side of the support, an emulsion layer was coated to reach a final silver ratio of 4.3 g/m^2. At the same time, emulsion protective layer was provided on the emulsion layer and dried using each of protective layer solutions P-1 through P-8 while adding formalin as a hardener under the conditions shown in Table 2 to prepare samples A-1 through A-17.

Table 2

Sample A	Emulsion layer protective layer	Backing side		Drying conditions	Surface smoothness degree mmHg		
		Protective layer	Amount of matting agent mg/m^2		Emulsion layer side	Backing layer side	
1	P-5	B-2a	150	B	42	300	Comparative
2	P-1	B-2b	40	A	10	100	Comparative
3	P-2	B-2b	40	A	35	100	Comparative
4	P-3	B-2b	40	A	25	100	Inventive
5	P-4	B-2b	40	A	30	100	Inventive
6	P-5	B-2b	40	A	38	100	Inventive
7	P-6	B-2b	40	A	65	100	Inventive
8	P-7	B-2b	40	A	40	100	Inventive
9	P-8	B-2b	40	A	45	100	Inventive
10	P-1	B-2b	40	B	13	100	Comparative
11	P-2	B-2b	40	B	42	100	Comparative
12	P-3	B-2b	40	B	34	100	Inventive
13	P-4	B-2b	40	B	39	100	Inventive
14	P-5	B-2b	40	B	49	100	Inventive
15	P-6	B-2b	40	B	80	100	Inventive
16	P-7	B-2b	40	B	51	100	Inventive
17	P-8	B-2b	40	B	53	100	Inventive

The surface smoothnesses were measured using the above-mentioned SM-6B, produced by Toei Denshi Kogyo KK, at 23° C and 48% humidity after moisture adjustment under the same conditions for 2 hours.

These samples were exposed while keeping the emulsion face of each sample in close contact with an original using a roomlight type printer P-605FS (produced by Dainippon Screen) for a varying exhaust time for vacuum contact, and then processed. Unevenness of the image density due to poor contact was visually evaluated.

The original, of 610 x 508 mm size, was prepared by superposing three sheets of polyester film for mounting and a screen tint having a dot area of 10% (film face was directed to the light source side) from the light source side.

Transparency loss and top-and-back differentiability were evaluated with respect to samples processed without exposure. Pinholes were examined after exposure to reach a density of 3.0 while keeping the emulsion face of the sample in close contact with a sheet of film for mounting, followed by processing. These characteristics were all evaluated in 5 grades, with a score of 5 assigned to best results and scores of 2 or less assigned to practical problems.

Processing was carried out using the following developer and fixer using an automatic processing machine GR-27 (produced by Konica Corporation) at 28°C for 30 seconds. The results are shown in Table 3.

Developer	
Composition A	
Pure water (ion exchanged water)	150 mℓ
Disodium ethylenediaminetetraacetate	2 g
Diethylene glycol	50 g
Potassium sulfite (55% w/v aqueous solution)	100 mℓ
Potassium carbonate	50 g
Hydroquinone	15 g
5-methylbenzotriazole	200 mg
1-phenyl-5-mercaptotetrazole	30 mg
Potassium hydroxide was added in an amount necessary to adjust the pH of the solution to 10.9.	
Potassium bromide	4.5 g
Composition B	
Pure water (ion exchanged water)	3 mℓ
Diethylene glycol	50 g
Disodium ethylenediaminetetraacetate	25 mg
Acetic acid (90% aqueous solution)	0.3 mℓ
5-nitroindazole	110 mg
1-phenyl-3-pyrazolidone	500 mg

The above-mentioned compositions A and B were dissolved in 500 ml of water in this order and diluted with water to reach a final quantity of 1 ℓ to prepare a developer.

Fixer	
Composition A	
Ammonium thiosulfate (72.5% w/v aqueous solution)	230 mℓ
Sodium sulfite	9.5 g
Sodium acetate trihydrate	15.9 g
Boric acid	6.7 g
Sodium citrate dihydrate	2 g
Acetic acid (90% w/w aqueous solution)	8.1 mℓ
Composition B	
Pure water (ion exchanged water)	17 mℓ
Sulfuric acid (50% w/w aqueous solution)	5.8 g
Aluminum sulfate (8.1% w/w aqueous solution as $A\ell_2O_3$)	26.5 g

The above-mentioned compositions A and B were dissolved in 500 mℓ of water in this order and diluted with water to reach a final quantity of 1ℓ to yield a fixer. This fixer had a pH of about 4.3.

Table 3-1

Sample A	Exhaust time (sec)	Contact unevenness	Pinholes	Transparency loss	Top/back differentiability	
1	16	2	4	4	2	Comparative
	8	1	4			
	4	1	4			
2	16	4	5	5	4	Comparative
	8	2	5			
	4	1	5			
3	16	4	4	4	2	Comparative
	8	3	4			
	4	2	4			
4	16	4	5	4	4	Inventive
	8	3	5			
	4	3	5			
5	16	4	5	4	4	Inventive
	8	4	5			
	4	3	5			
6	16	4	4	4	5	Inventive
	8	4	4			
	4	3	4			
7	16	5	3	3	5	Inventive
	8	4	3			
	4	3	3			

Table 3-2

Sample A	Exhaust time (sec)	Contact unevenness	Pinholes	Transparency loss	Top/back differentiability	
8	16	4	4	4	3	Inventive
	8	3	4			
	4	3	4			
9	16	4	4	4	4	Inventive
	8	4	4			
	4	3	4			
10	16	4	5	5	4	Comparative
	8	2	5			
	4	2	5			
11	16	5	5	5	2	Comparative
	8	4	5			
	4	3	5			
12	16	5	5	5	4	Inventive
	8	4	5			
	4	4	5			
13	16	5	5	5	4	Inventive
	8	5	5			
	4	4	5			
14	16	5	5	5	5	Inventive
	8	5	5			
	4	4	5			

Table 3-3

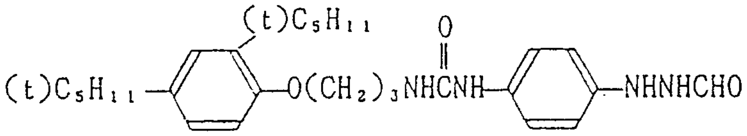
Sample A	Exhaust time (sec)	Contact unevenness	Pinholes	Transparency loss	Top/back differentiability	
15	16	5	4	4	5	Inventive
	8	5	4			
	4	4	4			
16	16	5	5	5	3	Inventive
	8	4	5			
	4	4	5			
17	16	5	4	5	4	Inventive
	8	5	4			
	4	4	4			

Example 2

A hydrazine compound (HD) was used as a contrast raising agent in place of the tetrazolium compound T used in Example 1.

Results similar to those obtained in Example 1 were obtained. Processing was carried out with the following Developer B at 38° C for 20 seconds.

Compound (HD)



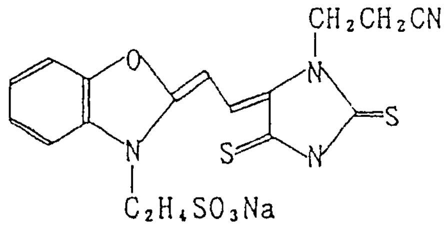
Developer B	
Hydroquinone	45.0 g
N-methyl-p-aminophenol 1/2 sulfate	0.8 g
Sodium hydroxide	15.0 g
Potassium hydroxide	55.0 g
5-sulfosalicylic acid	45.0 g
Boric acid	35.0 g
Potassium sulfite	110.0 g
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	6.0 g
5-methylbenzotriazole	0.6 g
n-butyl diethanolamine	15.0 g

Water was added in an amount necessary to reach a total quantity of 1 ℓ (pH = 11.6).

Example 3

Samples of negative film for dark room working were prepared using the following emulsion: The emulsion was prepared by adding the following sensitizing dye (C) at the time of chemical sensitization to an emulsion obtained in the same manner as in Example 1 except that the pentabromorhodate content was 25 µg per 60 g silver nitrate and the silver bromide content was 25% at the preparation of silver chlorobromide emulsion. Each sample was subjected to exposure through the same original as in Example 1 using a tungsten lamp. The same experiment as in Example 1 except for these aspects was conducted and exactly the same results were obtained.

Sensitizing dye (C)



Example 4

A high-sensitivity negative film for roomlight working was prepared as follows:

Preparation of samples

In an acidic atmosphere at pH of 3.0 in the presence of nitric acid, while maintaining a silver electrode potential (EAg) of 170 mV, the following solution B was added to the following solution A at a feed rate shown in the following Table 4, and they were mixed together by the controlled double jet method using 1 N NaCℓ to control the EAg value. At the same time, the following solution C was added at the same reaction temperature and same feed rate as those for solution B until 2 minutes after initiation of addition, and then at a feed rate 0.99 time the starting feed rate, while controlling the EAg with 1 N NaCℓ to yield silver halide emulsions a, b, c, d and e shown in Table 4.

Solution A	
Gelatin	5.6 g
10% ethanol solution of sodium salt of polyisopropylene-polyethyleneoxydisuccinate	0.56 mℓ
Sodium chloride	0.12 g
Concentrate nitric acid	0.43 mℓ
Distilled water	445 mℓ

Solution B	
Silver nitrate	60 g
Concentrate nitric acid	0.208 mℓ
Distilled water	85.2 mℓ

Solution C	
Gelatin	3 g
10% ethanol solution of sodium salt of polyisopropylene-polyethyleneoxydisuccinate	0.3 mℓ
Potassium bromide	4.2 g
Sodium chloride	18.6 g
1% aqueous solution of $Na_3RhC\ell_6$	0.02 mℓ
Distilled water	83.7 mℓ

Solution D	
Gelatin 1.4 g 10% ethanol solution of sodium salt of polyisopropylene-polyethyleneoxydisuccinate Distilled water	0.14 mℓ 48.8 mℓ

Table 4

Emulsion number		a	b	c	d	e
Reaction temperature		30°C	34°C	40°C	40°C	50°C
		Feed rate mℓ/min				
Solution B addition time min	0	11.74	11.74	17.07	1.06	1.06
	2	11.74	11.74	17.07	1.06	1.06
	3	11.93	11.93	17.36	1.08	1.08
	4	12.14	12.14	17.66	1.10	1.10
	5	12.34	12.34	17.95	1.11	1.11
	6	12.55	12.55	18.25	1.13	1.13
	7	12.75	12.75	18.55	1.15	1.15
	8	12.96	12.96	18.86	1.17	1.17
	9			19.16	1.19	1.19
	10			19.47	1.21	1.21
	11			19.47	1.23	1.23
	14				1.29	1.29
	18				1.37	1.37
	22				1.45	1.45
	26				1.54	1.54
	30				1.62	1.62
	35				1.74	1.74
	40				1.85	1.85
	45				1.98	1.98
	50				2.10	2.10
	55				2.23	2.23
	60				2.36	2.36
Average grain size of the obtained silver halide grains		0.06 µm	0.075 µm	0.095 µm	0.20 µm	0.30 µm

The average silver halide grain size of each obtained silver halide emulsion is shown in Table 4. Each silver halide emulsion had a silver chloride content of 90 mol%, a rhodium content of 2 x 10^{-6} mol per mol silver halide and a degree of monodispersibility of 8 to 15%.

EAg was measured using a metallic silver electrode and a double junction type saturated Ag/AgCℓ reference electrode.

A variable-flow-rate roller tube constant discharge pump was used to add solutions B and C.

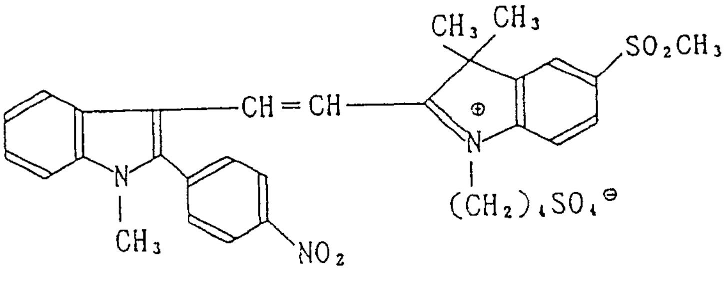
During addition, emulsion was sampled and observed by electron microscopy for the absence of newly formed grains to confirm that the feed rate did not exceed the critical growth rate for the system.

To each of emulsions a through e thus prepared, 200 mg per mol silver halide of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene was added. This mixture was adjusted to a pH of 5.7 with sodium carbonate, followed by the addition of solution D. Then, each silver halide emulsion was washed and desalted in accordance with an ordinary method. The emulsion was subjected to sulfur sensitization after adding 58 mg per mol silver halide of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene and 150 mg of potassium bromide. After sulfur sensitization, 570 mg per mol silver halide of 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene as a stabilizer and 25 g of gelatin were added to the emulsion. Then, the following additives were added to prepare emulsion layer coating solutions. Using exactly the same protective layer coating solutions, backing layer coating solution and backing protective layer coating solution as those in Example 1, samples Xa1 through Xa18, Xb1 through Xb18, Xc1 through Xc18, Xd1 through Xd18 and Xe1 through Xe18 to be evaluated were prepared. The alphabet i in Xi represents the emulsion type used (see Table 4).

The coating amount of silver was 3.5 g/m^2.

Emulsion layer coating solution additives	
Saponin	100 mg/m^2
Potassium bromide	3 mg/m^2
Desensitizing dye DS-1	1 mg/m^2
Sodium hydroxide	10 mg/m^2
Tetrazolium compound T	45 mg/m^2
Sodium dodecybenzenesulfonate	21 mg/m^2
Butyl acrylate-styrene-acrylic acid copolymer latex	1 g/m^2
5-methylbenzotriazole	10 mg/m^2
5-phenyl-1-mercaptotetrazole	11.5 mg/m^2
2-mercaptobenzimidazole-5-sulfonic acid	1 mg/m^2
Benzyl-triphenylphosphonium chloride	5 mg/m^2
Compound (M)	5.8 mg/m^2

DS-1

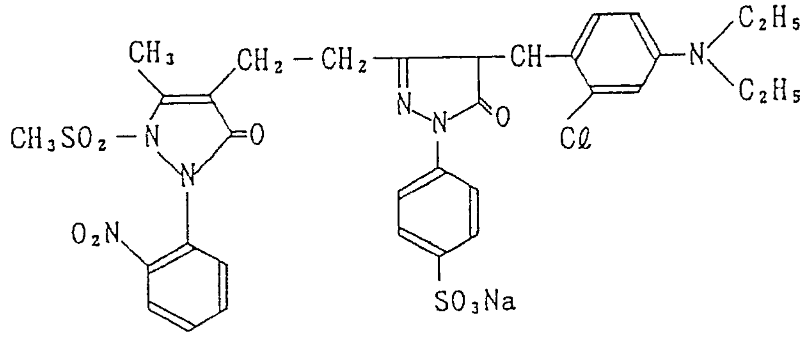


Samples were processed in the same manner as in Example 1 except that an ultraviolet cut filter Dialight P-1001 (produced by Mitsubishi Rayon) having a thickness of 2 mm was inserted between the light source and the surface glass of the roomlight type printer of Example 1. Results similar to those shown in Table 3 in Example 1 were obtained.

Example 5

Samples Y-1 through Y-18 were obtained in the same manner as in Example 4 except that the desensitizing dye DS-1 was eliminated and the tetrazolium compound T in the emulsion coating solution was replaced by a hydrazine compound (HD) at 10 mg/m^2 and the following compound (O) was added to the emulsion protective layer coating solution at 20 mg/m^2.

Compound (O)



The same evaluation procedure as Example 4 was followed except that development was carried out using developer B at 38 °C for 20 seconds. Similar results to those in Example 4 were obtained.

Example 6

Samples of direct positive silver halide photographic light-sensitive material were prepared as follows:

To an aqueous solution of gelatin at 55 °C having a pH of 2, an aqueous solution of gelatin containing 25 mg per mol silver of a rhodium trichloride.3NaCℓ complex salt and 2.5 mols of potassium bromide and another aqueous solution of 2.5 mol of silver nitrate were added by the double jet method over a period of 70 minutes while controlling the silver potential at 140 mV and the pH at 2 in an ion amount corresponding to grain growth.

Upon completion of mixing, the pH was increased to 5.5, after which the water-soluble salts were removed by ordinary coagulation, followed by the addition of gelatin to prepare a monodisperse silver bromide emulsion having an average grain size of 0.2 µm.

Preparation of emulsion coating solution E_1

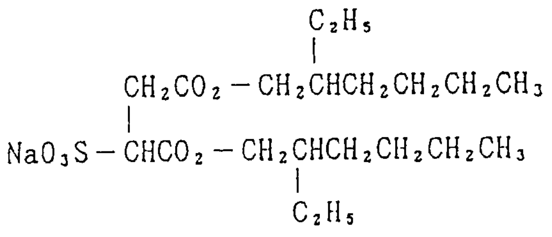
After the monodisperse silver bromide emulsion described above was adjusted to a pH of 7.5 by the addition of sodium carbonate, 12 mg per mol silver halide of thiourea dioxide was added, followed by ripening at 65 °C to cause fogging until maximum photographic characteristics was obtained. Then, the temperature was reduced to 40 °C, and 6 mg per mol silver halide of chloroauric acid was added to prepare an emulsion E_1.

Preparation of protective layer solution for emulsion layer

A protective layer was formed as follows:

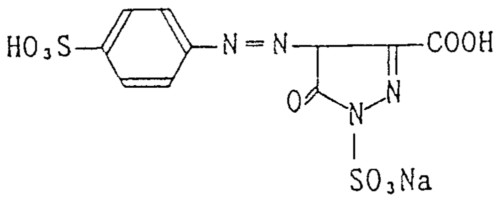
Pure water of 10ℓ was added to 1 kg of gelatin. After swelling, the gelatin was dissolved with heating. Then, 66 g of the following compound (Q-2) as a dye and 500 mℓ of an aqueous solution of the following compound (Q-1) as a coating aid were added in gelatin, and 10 mg of the following compound (Q-3) as a dye was added. To this solution, irregular-shaped silica as a matting agent was added as shown in Table 1 of Example 1 to yield protective layer coating solutions R-1 through R-8.

Compound (Q-1)

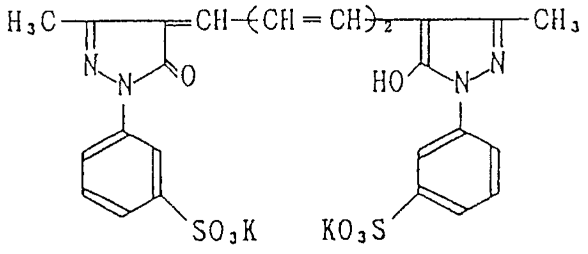


$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad C_2H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\quad CH_2CO_2-CH_2CHCH_2CH_2CH_2CH_3 \\ \qquad\quad | \\ NaO_3S-CHCO_2-CH_2CHCH_2CH_2CH_2CH_3 \\ \qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad C_2H_5 \end{array}$$

Compound (Q-2)



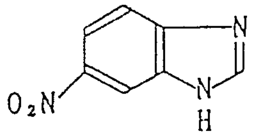
Compound (Q-3)



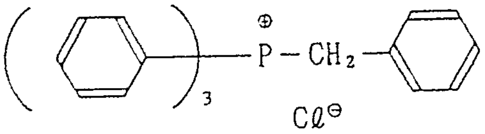
Preparation of emulsion coating solution E_2

To emulsion E_1, 560 mg per mol silver halide of the following compound (Q-4) and 8.5 g of the following compound (Q-5) as a latex polyethylene oxide compound, 280 mg of the above-mentioned compound (C-6) and 5.6 g of dextrin were added in this order, after which an emulsion coating solution E_2 was prepared while maintaining a viscosity of 15 cp at 35° C with a thickener.

Compound (Q-4)



Compound (Q-5)



Preparation of backing layer coating solution B-3

Coating solution B-3 was prepared in the same manner as in the backing coating solution B-1 except that 5 mg per gram gelatin of Phenidone was added in place of compound (C-6) and pH was adjusted to 5.4 with citric acid.

Preparation of backing protective layer coating solutions B-4a and 4b

Protective layer coating solutions B-4a and 4b were prepared in the same manner as in the protective film coating solutions B-2a and 2b described above except that no mucochloric acid was added.

Preparation of samples

Each of the coating solutions described above was coated on either side and then the other side of a subbed polyethylene terephthalate film having the thickness of 100 μm in the combinations shown in Table 4 to prepare the samples shown in Table 4. On either side of the subbed support, a backing base layer was formed using solution B-3 to reach a dry weight of gelatin of 2 g/m^2. At the same time, a backing protective layer was formed and dried on the backing layer by coating protective layer coating solutions B-4a and b to reach a dry weight of gelatin of 1 g/m^2. Then, on the other side of the support, an emulsion layer was coated to reach a dry weight of gelatin of 1.5 g/m^2 and a silver coating amount of 4.3 g/m^2. An emulsion protective film layer was formed thereon by coating protective film solutions R1 through R8 to reach a dry weight of gelatin of 1 g/m^2. Samples D1 through D17 were prepared while adding formalin as a hardener. The same drying conditions as A and B in Example 1 were used as shown in Table 5.

These samples were processed and evaluated in the same manner as in Example 1. Since samples D1 through D17 were direct-positive films, an original having the same structure as in Example 1 and having a screen tint dot area of 90% was used. Also, to evaluate transparency loss, an amount of exposure was chosen so that a minimum density was obtained. Mat pinholes were evaluated with respect to the samples processed without exposure. The processing solutions and conditions were the same as those in Example 1. The results are shown in Table 6.

Table 5

Sample D	Emulsion layer protective layer coating solution R	Backing side		Drying conditions	Surface smoothness degree mmHg		
		Protective layer coating solution	Amount of matting agent mg/m^2		Emulsion layer side	Backing side	
1	5	4a	150	B	40	300	Comparative
2	1	4b	40	A	11	100	Comparative
3	2	4b	40	A	36	100	Comparative
4	3	4b	40	A	24	100	Inventive
5	4	4b	40	A	30	100	Inventive
6	5	4b	40	A	39	100	Inventive
7	6	4b	40	A	63	100	Inventive
8	7	4b	40	A	39	100	Inventive
9	8	4b	40	A	42	100	Inventive
10	1	4b	40	A	12	100	Comparative
11	2	4b	40	A	43	100	Comparative
12	3	4b	40	A	36	100	Inventive
13	4	4b	40	A	42	100	Inventive
14	5	4b	40	A	45	100	Inventive
15	6	4b	40	A	81	100	Inventive
16	7	4b	40	A	50	100	Inventive
17	8	4b	40	A	52	100	Inventive

Table 6-1

Sample D	Exhaust time	Contact unevenness	Pinholes	Transparency loss	Top/back surface differentiability	
1	16	2	4	4	2	Comparative
	8	1	4			
	4	1	4			
2	16	3	5	5	4	Comparative
	8	1	5			
	4	1	5			
3	16	3	4	4	2	Comparative
	8	3	4			
	4	2	4			
4	16	4	5	4	4	Inventive
	8	3	5			
	4	3	5			
5	16	4	5	4	4	Inventive
	8	4	5			
	4	3	5			
6	16	4	4	4	5	Inventive
	8	4	4			
	4	3	4			
7	16	5	4	3	5	Inventive
	8	4	4			
	4	3	4			

Table 6-2

Sample D	Exhaust time	Contact unevenness	Pinholes	Transparency loss	Top/back surface differentiability	
8	16	4	4	4	3	Inventive
	8	3	4			
	4	3	4			
9	16	4	4	4	4	Inventive
	8	4	4			
	4	3	4			
10	16	3	5	5	4	Comparative
	8	1	5			
	4	1	5			
11	16	5	5	5	2	Comparative
	8	4	5			
	4	3	5			
12	16	5	5	5	4	Inventive
	8	4	5			
	4	4	5			
13	16	5	5	5	4	Inventive
	8	5	5			
	4	4	5			
14	16	5	5	5	5	Inventive
	8	5	5			
	4	5	5			

Table 6-3

Sample D	Exhaust time	Contact unevenness	Pinholes	Transparency loss	Top/back surface differentiability	
15	16	5	4	4	5	Inventive
	8	5	4			
	4	4	4			
16	16	5	5	5	3	Inventive
	8	4	5			
	4	4	5			
17	16	5	5	5	4	Inventive
	8	5	4			
	4	4	4			

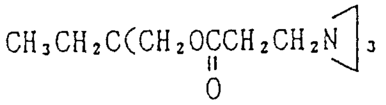
Example 7

After corona discharge at an energy level of 8 w/m^2 min, a subbed polyethylene terephthalate film was coated with an antistatic solution having the following composition to reach the following coating amount at a speed of 30 m/min using a roll fit coating pan and an air knife.

Water-soluble electroconductive polymer (A)	0.6 g/m^2
Inventive hydrophobic polymer particles (B)	0.4 g/m^2
Nonionic surfactant (Ao)	0.004 g/m^2

The hydrophobic polymer particles (B) were used in the form of a latex in dispersion in the nonionic surfactant.

Hardener (H)



$CH_3CH_2C(CH_2OC(=O)CH_2CH_2N\langle)_3$

0.1 g/m^2

After drying at 90° C for 2 minutes, heat treatment was carried out at 140° C for 90 seconds. This antistatic layer was coated with gelatin at 2.0 g/m^2 and a haze test was carried out. Formalin and 2,4-dichloro-6-hydroxy-S-triazine sodium were used as gelatin hardeners. The results are shown in Table 7.

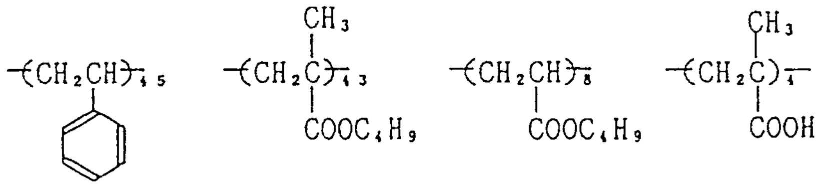
Haze test

The haze of the film support was measured using a turbidometer model T-2600DA produced by Tokyo Denshoku KK and is expressed in percent ratio. Lower percentage of the value indicates lower haze.

Table 7

No.	Water-soluble electroconductive polymer (A)	Hydrophobic polymer particles (B)	Nonionic surfactant (Ao)	Haze	
1	3	a	-	80	Comparative
2	3	1	1	90	Inventive
3	5	2	2	95	Inventive
4	7	2	2	93	Inventive
5	9	3	2	95	Inventive
6	13	3	9	95	Inventive
7	18	6	15	92	Inventive
8	20	2	2	90	Inventive
9	21	8	19	94	Inventive
10	22	8	28	93	Inventive
11	24	2	2	93	Inventive
12	41	3	9	92	Inventive

a: Polymer having the following structure:



From the results shown in Table 7, it is evident that the samples prepared in accordance with the present invention are excellent in haze.

Example 8

An emulsion coating solution containing the same emulsion and latex as those in Example 1, emulsion protective layer coating solutions P-1 through P-8, a backing coating solution B-1 and a backing protective layer coating solution B-2b were prepared.

Preparation of samples

Using the subbed support the same as in Example 1 (hereinafter referred to as No. 0) and the subbed supports with an antistatic layer Nos. 2, 4 and 7 described in Table 7 of Example 7, backing layer coating solution B-1 and backing layer protective film coating solution B-2b were coated on either face of each support simultaneously.

On the opposite face of each support, the emulsion layer coating solution and layer protective film coating solutions P-1 through P-8 were coated by the simultaneous multiple layer coating method to prepare evaluation samples E-1 through E-32 shown in Table 3. Coating and drying conditions at the time of emulsion layer side coating were settled so that the surface temperature became 17° C when the water-gelatin ratio by weight became 400%.

The coating amount of gelatin was 2.0 g/m^2 for the backing layer, 1.5 g/m^2 for the backing protective layer, 2.0 g/m^2 for the emulsion layer and 1.1 g/m^2 for the emulsion protective layer, and the coating amount of silver was 3.5 g/m^2.

Surface smoothness degree was measured using SM-6B produced by Toei Denshi Kogyo KK at 23° C and 48% RH after 2 hours of moisture adjustment under the same conditions after development of the unexposed sample under the conditions described below.

Dust adhesion test

After samples were kept at 23° C and 48% RH for 2 hours for moisture adjustment, the surface of emulsion coated side of sample was thrice rubbed with a rubber roller for printer. Each sample was kept standing for 5 seconds with its emulsion side facing the upper surface of a desk spread with cigarette ash at a position 2 cm above the upper surface of the desk while maintaining the emulsion side in parallel with the upper surface of the desk, and the degree of ash adhesion was evaluated in 5 grades.

Surface resistivity storage stability test

Unexposed samples were developed under the conditions described below and stored under the following conditions:
Storage conditions I: 23° C and 55% RH, 3 days
Storage conditions II: 23° C and 55% RH, 3 hours, followed by storage in a sealed moisture-proof bag at 55° C for 3 days.

The surface resistivity of each sample stored under each set of conditions was measured at 23° C and 20% RH after moisture adjustment under the same conditions.

Evaluation of blurring of printed image

An original of a screen tint with a dot area of 10% was placed on a printer P-627FM for roomlight work (produced by Dainippon Screen) while keeping its film face in the direction of the light source side. Commercially available tissue paper was teared by hand above this original, and the resulting dust was spread uniformly over the original. The emulsion surface of each sample was brought into close contact with this original and subjected to exposure for an exhausion time of 8 seconds and processed using the same processing solutions as those in Example 1 under the following conditions. The obtained sample was evaluated visually in 5 grades according to the degree of blurring of printed image.

Developing conditions		
Process	Temperature (° C)	Duration (sec)
Development	34	15
Fixation	34	15
Washing	Normal temperature	10

The obtained results are shown in table 3.

Samples were ranked in the following 5 grades.

1: No practical use.
2: The same level as with currently available products.
3: Better than grade 2, but no practical differences.
4: Improved in comparison with commercially available products and useful.

5: Better than grade 4 and very useful.

Table 8-1

Sample E	Emulsion protective layer P number	Support number	Emulsion layer surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity ($\Omega \cdot cm^{-2}$)		
							No storage	Storage I	Storage II
1	1	0	10	4	2	2	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
2	2	0	35	2	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
3	3	0	25	4	3	3	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
4	4	0	30	4	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
5	5	0	38	5	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
6	6	0	65	5	3	5	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
7	7	0	40	3	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
8	8	0	45	4	3	5	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
9	1	2	10	4	3	2	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
10	2	2	35	2	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
11	3	2	25	4	4	3	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$

Table 8-2

Sample E	Emulsion protective layer P number	Support number	Emulsion layer surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity ($\Omega \cdot cm^{-2}$)		
							No storage	Storage I	Storage II
12	4	2	30	4	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
13	5	2	38	5	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
14	6	2	65	5	4	5	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
15	7	2	40	3	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
16	8	2	45	4	4	5	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
17	1	4	10	4	5	2	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
18	2	4	35	2	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
19	3	4	25	4	5	3	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
20	4	4	30	4	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
21	5	4	38	5	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
22	6	4	65	5	5	5	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$

Table 8-3

Sample E	Emulsion protective layer P number	Support number	Emulsion layer surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity (Ω•cm^{-2})		
							No storage	Storage I	Storage II
23	7	4	40	3	5	4	4x10^{10}	5x10^{10}	4x10^{11}
24	8	4	45	4	5	5	4x10^{10}	5x10^{10}	4x10^{11}
25	1	7	10	4	4	2	2x10^{10}	3x10^{10}	7x10^{11}
26	2	7	35	2	5	4	2x10^{10}	3x10^{10}	7x10^{11}
27	3	7	25	4	5	3	2x10^{10}	3x10^{10}	7x10^{11}
28	4	7	30	4	5	4	2x10^{10}	3x10^{10}	7x10^{11}
29	5	7	38	5	5	4	2x10^{10}	3x10^{10}	7x10^{11}
30	6	7	65	5	5	5	2x10^{10}	3x10^{10}	7x10^{11}
31	7	7	40	3	5	4	2x10^{10}	3x10^{10}	7x10^{11}
32	8	7	45	4	5	5	2x10^{10}	3x10^{10}	7x10^{11}

Example 9

A hydrazine compound (HD) was used as a contrast raising agent in place of the tetrazolium compound T used in Example 8.

Similar results to those obtained in Example 8 were obtained. The same developing conditions were used as those in Example 8.

Example 10

Samples were prepared in the same manner as in Example 8 except that the same emulsion for negative film for dark room processing as in Example 3 was used. Samples were evaluated in the same manner as in Example 1 except that exposure was carried out under the same conditions as in Example 3. The same results as in Example 8 were obtained.

Example 11

Samples of direct-positive silver halide photographic light-sensitive material was prepared.

The same emulsion E_1 as in Example 6 was prepared, and a protective layer was formed as follows:

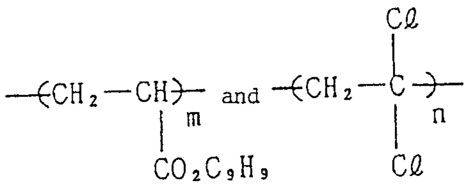
Preparation of emulsion layer protective layer coating solutions

Emulsion protective layer coating solutions S-1 through S-8 were prepared in the same manner as in Example 6 except that the compounds (Q-1), (Q-2) and (Q-3) in the emulsion layer protective layer coating solutions in Example 6 were replaced with the compounds (C-1), (C-2) and (C-3) described above, respectively.

Preparation of emulsion coating solution E_3

After 560 mg per mol silver halide of the following compound (Q-9), 8.5 g of the following compound (Q-10) as a latex polyethylene oxide compound, 280 mg of the above-mentioned compound (C-6) and 5.6 g of dextrin were added to emulsion E_1 to prepare emulsion coating solution E_3. Viscosity of the coating solution was adjusted to 15 cp at 35° C with a thickener.

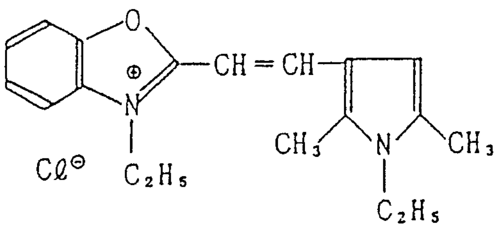
Compound Q-9



$$-\!\left(CH_2-\underset{\textstyle CO_2C_9H_9}{CH}\right)_m\!- \text{ and } -\!\left(CH_2-\underset{\textstyle C\ell}{\overset{\textstyle C\ell}{C}}\right)_n\!-$$

Copolymer latex of and wherein m:n = 1:1.

Compound Q-10



Preparation of backing layer coating solution B-3

The same coating solution B-3 as in Example 6 was prepared.

Preparation of backing protective layer coating solution B-4

The same protective film coating solution B-4b as in Example 6 was prepared.

Preparation of samples

Using the same support as in Example 8, the samples shown in Table 4 were prepared. On either surface of the subbed support, a backing base layer was formed using coating solution B-3 to reach a dry weight of gelatin of 2 g/m^2. At the same time, a backing protective layer was formed and dried thereon by coating protective layer solution B-4 to reach a dry weight of gelatin of 1 g/m^2. Then, on the other face of the support, an emulsion layer and a protective layer were simultaneously coated and dried. In the emulsion layer, the dry weight of gelatin was 1.5 g/m^2 and a silver coating amount was 4.3 g/m^2. The dry weight of gelatin in the protective layer was 1 g/m^2 in which formalin was added as a hardener. Thus samples F-1 through F-8 were prepared in each of which protective layer coating solution S-1 through S-8 were used, respectively.

Then, using the subbed supports Nos. 2, 4 and 7 of Example 7, backing layer coating solution B-3 and backing protective film coating solution B-4B were coated thereon simultaneously, followed by simultaneous multiple layer coating of emulsion coating solution E_3 and emulsion protective layer coating solutions S-1 through S-8 under the same conditions as in Example 8 to prepare samples F-9 through F-32. The amounts of gelatin and silver in each layer were the same as those in F-1 through F-8.

These samples were processed and evaluated in the same manner as in Example 8. However, since the samples F-1 through F-32 were direct positive films, an original having a screen tint dot area of 90% was used. The developer formulation and developing conditions were the same as in Example 8.

The results are shown in Table 9.

Table 9-1

Sample F	Emulsion protective layer R	Subbed base number	Emulsion surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity ($\Omega \cdot cm^{-2}$)		
							No storage	Storage I	Storage II
1	1	0	11	4	2	2	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
2	2	0	36	2	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
3	3	0	24	4	3	3	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
4	4	0	30	4	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
5	5	0	39	5	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
6	6	0	63	5	3	5	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
7	7	0	39	3	3	4	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
8	8	0	42	4	3	5	$2x10^{13}$	$2x10^{13}$	$3x10^{13}$
9	1	2	11	4	3	2	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
10	2	2	36	2	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
11	3	2	24	4	4	3	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$

Table 9-2

Sample F	Emulsion protective layer R	Subbed base number	Emulsion surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity ($\Omega \cdot cm^{-2}$)		
							No storage	Storage I	Storage II
12	4	2	30	4	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
13	5	2	39	5	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
14	6	2	63	5	4	5	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
15	7	2	39	3	4	4	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
16	8	2	42	4	4	5	$3x10^{10}$	$4x10^{10}$	$2x10^{11}$
17	1	4	11	4	5	2	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
18	2	4	36	2	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
19	3	4	24	4	5	3	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
20	4	4	30	4	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
21	5	4	39	5	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$
22	6	4	63	5	5	5	$4x10^{10}$	$5x10^{10}$	$4x10^{10}$

Table 9-3

Sample F	Emulsion protective layer R	Subbed base number	Emulsion surface smoothness degree	Top/back surface differentiability	Dust adhesion	Printing unsharpness	Surface resistivity ($\Omega \cdot cm^{-2}$)		
							No storage	Storage I	Storage II
23	7	4	39	3	5	4	$4x10^{10}$	$5x10^{10}$	$4x10^{11}$
24	8	4	42	4	5	5	$4x10^{10}$	$5x10^{10}$	$4x10^{11}$
25	1	7	11	4	4	2	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
26	2	7	36	2	5	4	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
27	3	7	24	4	5	3	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
28	4	7	30	4	5	4	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
29	5	7	38	5	5	4	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
30	6	7	65	5	5	5	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
31	7	7	40	3	5	4	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$
32	8	7	45	4	5	5	$2x10^{10}$	$3x10^{10}$	$7x10^{11}$

Claims

1. A silver halide photographic light-sensitive material comprising
a support,
a hydrophilic colloid layer and a silver halide emulsion layer provided on a surface of said support and
a hydrophilic colloid layer provided on the back surface of said support opposite to the surface the emulsion provided thereon,
wherein the layer arranged at the outermost portion of the emulsion provided side of the support contains
a first kind of irregular-shaped matting agent having a particle size of less than 4 μm in an amount of frpm 4 mg/m^2 to 80 mg/m^2, and
a second kind of regular-shaped or iregular-shaped matting agent having a size of not less than 4 μm in an amount of from 4 mg/m^2 to 80 mg/m^2, and
the outer surface of said layer arranged at the outermost portion of the emulsion provided side of the support has a surface smoothness degree of not less than 25 mmHg.

2. A material of claim 1, wherein the size of said first matting agent is within the range of from 1.0 μm to less than 4 μm.

3. A material of claim 1, wherein the size of said second matting agent is within the range of from 4 μm to 17 μm.

4. A material of claim 1, wherein the amounts of said first and second kinds of matting agents are each within the range of from 4 mg/m^2 to 30 mg/m^2.

5. A material of claim 1, wherein said surface smoothnes degree is with in the range of from 25 mmHg to 200 mmHg.

6. A material of claim 1, wherein said hydrophilic layer provided on the back side of said support contains a kind of gregular-shaped matting agent in an amount of from 4 mg/m^2 to 80 mg/m^2 and a kind of irregular-shaped matting agent in an amount of zero to 15 mg/m^2, and the smoothness degree of the outer surface of said hydrphilic layer is not more than 200 mmHg.

7. A material of claim 6, wherein said surface smoothness degree of said layer provided onthe back side of the saupport is within the range of from 25 mmHg to 200 mmHg.

8. A material of claim 1, wherein said hydrophilic layer provided on the back side of the support has a specific surface resistance of not more than 1.0×10^{12}, $\Omega \cdot cm^{-2}$.

9. A material of claim 8, wherein said specific surface resistance is not more than 0.8×10^{11} $\Omega \cdot cm^{-2}$.

10. A material of claim 1, wherein said support has an antistatic layer provided on the back side and said antistatic layer comprises a water-soluble electroconductive polymer, a hydrophobic polymer particle and a hardener.

11. A material of claim 10, wherein said hydrophobic polymer particle is dispersed in said water-soluble electroconductive polymer with a nonionic surfactant having three or more alkylene oxide groups.

12. A material of claim 10, wherein said water-soluble electroconductive polyer contains a sulfonic acid group, a sulfric ester group, a qurtanary ammonium group, a tertiary ammonium group or a polyethylene oxide group.

13. A material of claim 1, wherein said silver halide emulsion layer contains a tetrazolium comound or a hydrazin compound.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9656

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4 343 873 (S.SASAOKA) * claims 1, 8, 14 * – – –	1-13	G 03 C 1/95
Y	US-A-4 711 838 (N.E.GRZESKOWIAK) * column 4, lines 20 - 30 * – – –	1-7,13	
Y	US-A-4 225 665 (F.L.SCHADT) * abstract * – – –	8-12	
Y	US-A-3 411 907 (K.R.WHITMORE) * claim 1 * – – –	1-7	
A	EP-A-0 282 171 (MINNESOTA MINING AND MANUFACTURING CO) * the whole document * – – –	1-7	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 223 (P-597)(2670) 21 July 1987, & JP-A-62 038455 (MITSUBISHI PAPER MILLS LTD) 19 February 1987, * the whole document * – – – – –	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	27 November 90	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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